Volume XXVI. *June, 1908.* *Number 6.*

THE

PHYSICAL REVIEW.

DISTRIBUTED CAPACITY IN RESISTANCE BOXES.

By A. H. Taylor and E. H. Williams.

THE error introduced into alternating current precision measurements by the distributed capacity of the ordinary non-inductively wound coils of a resistance box is perhaps not generally appreciated. This error was brought particularly to the attention of one of us[1] in the course of some work with the differential A.C. galvanometer, and the evaluation of the distributed capacity in some typical cases was determined upon.

A substitution of the coil in question in one arm of an Anderson bridge, in the place of a coil practically free from inductance and capacity, offered a convenient method of attacking the problem. The equations of this bridge, taking into account residual inductances in all arms, have been given by Rosa and Grover[2] and, as they point out, residual capacities can be taken account of by considering them as equivalent to negative inductances.

The distributed capacity of an ordinary resistance coil is, we think we can safely state, not by any means entirely due to the bifilar winding and the compact space occupied by the coil. However, since these do have their effect, our ideal coils were wound on wooden frames about 12 cm. in diameter and 18 cm. high. The windings were bifilar; in fact they were braided together before wound. Consecutive turns were, however, separated 5 mm. The braiding insured that the coils were absolutely non-inductive, but it

[1] A. Trowbridge and A. H. Taylor, Phys. Rev., December, 1906.

[2] Bulletin of the Bureau of Standards, Vol. I., No. 3.

seemed possible that there might be some noticeable distributed capacity. In order to determine this, we used two identical 1,000-ohm coils of No. 40 Advance wire, alternately in an arm of the Anderson bridge. One coil was in air, the other in kerosene, which on account of its high dielectric constant, would have increased the capacity of one coil several fold. The balance of the bridge, as determined with a very sensitive A.C. galvanometer,[1] was not noticeably disturbed on substituting one coil for the other. This means that the distributed capacity of our ideal coils is so small that even when increased several fold it is neglible.

The equation of the Anderson bridge, as used by Rosa and Grover, is

$$L = cS\left[\frac{r(P+R)}{R} + P\right] + \alpha - \beta,$$

where α and β are terms involving the residual inductances l_1, l_2, etc., of the different branches. The term β is so small with any ordinary frequencies that it is entirely negligible. The other term is

$$\alpha = \frac{\mathrm{I}}{R}[l_1 S - l_2 R - l_3 Q + l_4 P].$$

The coils tested were alternated with ideal coils in the branch R, so that the portion of α of interest is

$$\frac{\mathrm{I}}{R}[-l_3 Q] = -l_3\frac{Q}{R}.$$

If l_2 is due to distributed capacity, considered as in parallel with the branch R; $l_2 = -R^2C'$ where C' is the value of the distributed capacity. Hence the change in the value of L on substituting a given coil for an ideal coil is $\Delta L = RQC'$.

Balance of the bridge was restored by changing r, whose distributed capacity scarcely affects the results. Moreover r was made up of small coils in series, giving very little capacity. The value of ΔL was thus determined from the change in r necessary to keep the bridge balanced when a given coil was substituted for an ideal coil. Due allowance was made for any slight differences existing between the resistances of the coils exchanged.

[1] A. H. Taylor, PHYS. REV., July, 1907.

TABLE I.

Wolff Boxes.

Box No.	Coil.	Resistance in Ohms.	ΔL in M.H.	Capacity C' M.F.
2894	1,000-ohm.	1,000.5	.517	.000517
2896	1,000 "	1,000.8	.57	.00057
2897	1st 1,000 "	1,000.7	.59	.00059
"	2d 1,000 "	1,000.9	.57	.00057
2898	1st 1,000 "	1,000.7	.53	.00053
"	2d 1,000 "	1,000.6	.53	.00053
2899	1,000 "	1,000.8	.59	.00059
2900	1,000 "	1,001.2	.577	.000577
2615	1st 1,000 "	1,000.5	.535	.000535
"	2d 1,000 "	1,000.4	.485	.000485

TABLE II.

Leeds and Northrup Coils.

Physics Box No.	Coil.	Resistance in Ohms.	ΔL in M.H.	Capacity in M.F.
1	1,000-ohm.	1,000.2	.074	.000074
3	1,000 "	1,000.2	.074	.000074
4	1,000 "	1,000.4	.077	.000077
6	1,000 "	1,000.0	.070	.000070

TABLE III.

Two 1,000-ohm Coils in Series.

Wolff Box No.	Coil.	Resistance in Ohms.	ΔL in M.H.	Capacity in M.F.
2894	1,000-ohm	1,000.5		
2896	1,000 "	1,000.8	.563	.000281
2894	1,000 "	1,000.5		
2899	1,000 "	1,000.9	.552	.000276
2896	1,000 "	1,000.8		
2899	1,000 "	1,000.9	.564	.000282
2897	1st 1,000 "	1,000.7		
"	2d 1,000 "	1,000.9	.563	.000281
2898	1st 1,000 "	1,000.7		
"	2d 1,000 "	1,000.6	.56	.00028
2900	1,000 "	1,001.2		
2898	1st 1,000 "	1,000.7	.586	.000293
2900	1,000 "	1,001.2		
2898	2d 1,000 "	1,006	.565	.000282
2615	1st 1,000 "	1,000.5		
"	2d 1,000 "	1,000.4	.528	.000264

Table I. gives the results obtained with the 1,000-ohm coils of boxes made by O. H. Wolff, Berlin. These coils are wound on brass, heavily coated with schellac, and baked very hard. Their capacity is relatively very large, and fairly consistent for different coils of the same size.

Table II. gives the values obtained from 1,000-ohm coils made by Leeds and Northrup, wound on wood and coated with shellac. The capacity is about one eighth as much as that of the Wolff coils.

By placing two coils of equal resistance and capacity in series, a resultant capacity of one half that of one coil should be obtained. Table III. shows the result of a series of such determinations, the capacity in this case being nearly one half of the value for single coils.

TABLE IV.

Two 1,000-ohm Coils in Parallel.

Wolff Box No.	Coil.	Resistance in Ohms.	ΔL in M.H.	Capacity in M.F.
2894	1,000-ohm			
2896	1,000 "	500.5	.554	.001108
2897	1st 1,000 "			
2898	1st 1,000 "	500.35	.572	.001144
2899	1,000 "			
2900	1,000 "	500.5	.576	.001152
2898	1st 1,000 "			
2899	1,000 "	500.6	.579	.001158
2898	2d 1,000 "			
2899	1,000 "	500.5	.554	.001108
2897	2d 1,000 "			
2898	1,000 "	500.6	.54	.001080
2896	1,000 "			
2900	1,000 "	500.5	.576	.001152

TABLE V.

500-ohm Coils Alone.

Wolff Box No.	Coil.	Resistance in Ohms.	αL in M.H.	Capacity in M.F.
2894	500-ohm	500.7	.084	.000168
2896	500 "	500.6	.080	.00016
2897	500 "	500.6	.080	.00016
2898	500 "	500.6	.108	.000216
2899	500 "	500.6	.080	.00016
2900	500 "	500.6	.080	.00016

TABLE VI.

Two 500-ohm Coils in Series.

Wolff Box No.	Coil.	Resistance in Ohms.	ωL in M.H.	Capacity in M.F.
2897	500-ohm	500.6		
2898	500 "	500.6	.09	.00009
2899	500 "	500.6		
2900	500 "	500.6	.108	.000108
2897	500 "	500.6		
2900	500 "	500.6	.091	.000091

TABLE VII.

2,000-ohm Coils Alone.

Wolff Box No.	Coil.	Resistance in Ohms.	ωL in M.H.	Capacity in M.F.
2615	2,000-ohm	2,000.6	1.225	.000612
2897	2,000 "	2,002.5	1.26	.000630
2898	2,000 "	2,001	.818	.000409

TABLE VIII.

2,000-ohm Coils in Parallel.

Wolff Box No.	Coil.	Resistance in Ohms.	ωL in M.H.	Capacity in M.F.
2615	2,000-ohm			
2698	2,000 "	1,000.4	1.047	.001047
2615	2,000 "			
2697	2,000 "	1,000.8	1.273	.001273
2697	2,000 "			
2698	2,000 "	1,000.9	1.075	.001075

TABLE IX.

1,000-ohm Coils Alone. Frequency, 114 Cycles.

Wolff Box No.	Coil.	Resistance in Ohms.	ωL in M.H.	Capacity in M.F.
2894	1,000-ohm	1,000.5	.487	.000487
2896	1,000 "	1,000.8	.491	.000491
2897	1st 1,000 "	1,000.7	.509	.000509
2897	2d 1,000 "	1,000.9	.512	.000512
2898	1st 1,000 "	1,000.7	.509	.000509
2898	2d 1,000 "	1,000.6	.508	.000508
2900	1,000 "	1,001.2	.536	.000536

The distributed capacity of 500-ohm coils was then measured, by substituting them in place of the two ideal 1,000-ohm coils in parallel. These gave values much less than the 1,000-ohm coils, as will be seen from the following table:

TABLE X.

2,000-ohm Coils Alone. Frequency, 114 Cycles.

Wolff Box No.	Coil.	Resistance in Ohms.	ωL in M.H.	Capacity in M.H.
2897	2,000-ohm	2,002.5	1.218	.000609
2898	2,000 "	2,001	.777	.000388

This shows clearly the advantage of building up a large resistance out of smaller units. Connecting two coils in parallel should double the capacity. This is shown in Table IV. Table V. gives the values for the distributed capacity of Wolff coils of 500 ohms, while Table VI. shows the effect of putting two such coils in series.

Table VII. shows that the capacity of the 2,000-ohm coils is but little larger than that of the 1,000-ohm, which leads to the suspicion that the effect is peculiar to the inner layers of the coils. This was verified later.

Table VIII. shows the effect of paralleling 2,000-ohm coils.

Up to this point all observations had been taken with a 60-cycle A.C. with very prominent third harmonics present in such a way as to give a very peaked wave. As a check on results a frequency of 114 cycles, with a fairly good wave form was now used. Table IX. gives the results for the 1,000-ohm Wolff coils, while Table X. refers to two of the 2,000-ohm coils.

Comparison with Tables I. and VII. shows the capacity as determined at the higher frequency to be uniformly lower.

The negative term β in the equations of Rosa and Grover is not of sufficient magnitude to account for this discrepancy, which is somewhat larger than the probable experimental error.

The problem of immediate interest was then to determine the cause of the high value for the distributed capacity of the Wolff coils.

Two coils were wound, one on a brass and one on a wooden core, otherwise exactly similar. The brass core gave slightly higher

values, but neither coil had a capacity much exceeding that of the Leeds and Northrup coils. The effect of shellac was to cause an enormous increase in capacity, due probably to electrolytic action. This can be obviated by baking the coils at about 120°, in the case of the one with the brass core, for several days, as the layer of schellac next to the brass core crusts over and dries very slowly.

One of the Wolff coils was then soaked in alcohol and baked repeatedly for several days, resulting in an appreciable lowering of the capacity, but leaving it still many times higher than the Leeds coils.

Our 1,000 coil wound on wood, in exactly the same manner as the Wolff coils, was of No. 36 Advance, and had a capacity of .00016 M.F. The Wolff coil was of a larger size wire, apparently No. 34 Manganin. A coil of No. 40 Advance gave a very small *negative* value for the distributed capacity, *i. e.*, the residual inductance exceeded the capacity. On the other hand, a coil made of No. 34 Advance gave a capacity of .00048 M.F., which compares with the Wolff coil which had been soaked in alcohol and baked (cap. .00045). The conclusions are apparent. In order to increase their ability to carry current, the Wolff coils are made of rather large, and hence long, wire. This large surface gives an abnormal value to the distributed capacity, which is still farther slightly increased by the fact that, in order to facilitate cooling, the coils are wound on brass cores, so that even after days of baking the inner layer of schellac does not dry thoroughly. This also slightly increases the capacity.

While these coils are excellent for D.C. work, it is evident that they possess a serious defect from the standpoint of precise A.C. measurements.

UNIVERSITY OF WISCONSIN,
February 24, 1908.

DETERMINATION OF THE SUSCEPTIBILITY OF COPPER AND TIN AND THEIR ALLOYS.

BY O. C. CLIFFORD.

THIS investigation was begun at the suggestion of Professor Michelson to determine, if possible, what function the magnetic susceptibility of an alloy of copper and tin is of the susceptibility of the constituents. As a result of the investigation a simple relation has been found between the susceptibility of the alloy and its per cent. composition. Furthermore the value of the susceptibility of copper and tin have been determined with an accuracy heretofore unattained, and the susceptibility of bismuth has been explored through a range of field strength much lower than that used in preceding investigations.

Fig. 1.

After spending considerable time in attempting to determine weak susceptibility by ballistic methods, the following torsional balance method was adopted. An electro-magnet, Fig. 1, with large bored pole pieces *N*–*S* placed vertically and with small poles *p*, inserted in the face of *N* and *S*, was used to produce the magnetic field. To the top of *N* was attached a tube with an adjustable head through which worked a slotted screw ending in a chuck for holding the torsional fiber attached to the spindle of the system *s*. *a* and *b* gave two horizontal movements for centering the test pieces *t* with reference to the poles *p*. *c* gave a vertical centering. When the clamping screw *d* was open, the whole system could be turned around by the large milled head. When *d* was clamped, a finer adjustment could be made by the tangent screw *e*. *m* was a mirror on the spindle which reflected a meter circular scale to a telescope. Fig. 2 shows the spindle of the

system which was suspended by a three mil phosphor bronze ribbon. This shaft was lowered into the tube and the taper just below the mirror fitted snugly into the system disk, Fig. 3. The shaft and disk were made of white celluloid as that material was found very free from iron, strongly diamagnetic and showed any dirt lodging upon it. The fact that it was diamagnetic tended to make it self centering, as the weakest part of the field was in the center of the holes through the large poles. The disk was provided with a collar about which a split inertia ring could be slipped and had two diametrical holes, 4.36 cm. apart, into which the bismuth test pieces, Fig. 4, *a*, actual size, could be slipped. These test pieces were the same diameter as the test coil used in exploring the field, so they had the same field through them as was measured by the coil. As the method was a repulsion one, the bismuth test pieces were always in place. Fig. 4, *b*, actual size, shows a test piece of other material, which was placed directly on top of the bismuth.

Fig. 2.

The current used to excite the field magnet was taken from storage cells. Connections were made in such a manner with dynamo and slide-wire resistance that the current through the field could be varied from .5 to 2 amperes and sent in either direction through the magnet. For change of

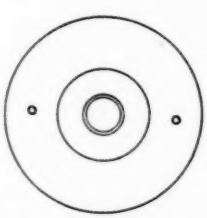


Fig. 3.

Fig. 4.

direction a double knife switch was used. Current determinations were all made by means of a Weston ammeter. As the absolute value of the current was not necessary, the ammeter was not calibrated.

METHOD OF TAKING READINGS.

The bismuth test pieces having been placed in position on the spool, they were raised or lowered by means of the nut on the slotted screw so that they were about midway between the small pole pieces. A lowering or raising of several millimeters caused no change in deflection, showing a fairly vertical field. By means of the two right angled sliding ways and the large milled head with the tangent screw for final adjustment, the pieces were then put in line with the small pole pieces and centered for the magnetic field, so that a movement of a millimeter or two on the circular scale would cause them to swing front or back, when the field was thrown on. In as much as it was impossible to bring the system of relatively large moment of inertia exactly to rest, the zero was taken by the method of oscillations. These were however never greater than one or two per cent. of the total deflection.

SOLUTION FROM THE READINGS.

If V is the volume of one of the test pieces, H the magnetic field strength at the point where equilibrium of forces exists, dH/dx the rate of change of magnetic field at this point and f the magnitude of the force acting upon the test piece,

$$f = kVH\, dH/dx.^1$$

k is the susceptibility and dx is taken in the direction of the arc. Solving this equation for k, we get

$$k = \frac{f}{VH\, dH/dx}.$$

THE DETERMINATION OF f.

To find the value in dynes of the force of restitution, it was first necessary to find the moment of torsion u of the fiber. This was obtained from oscillations. From t_1, the period of oscillation of the system alone, t_2 the period with an added inertia ring and K, the moment of inertia of the ring,

$$u = \frac{4\pi^2 K}{t_2^2 - t_1^2}.$$

[1] Fleming's Handbook, Vol. II., p. 491.

The force f acting on the test piece is obtained from the relation $fr/\vartheta = u$, where r is one half the distance between the test pieces and ϑ is the angular deflection in radians. To express ϑ in scale readings we have $\vartheta = d/2R$, where d is the deflection in cm. on the scale and R is the radius of the scale. Substituting back,

$$f = \frac{u\vartheta}{r} = \frac{ud}{2Rr} = \frac{4\pi^2 Kd}{2Rr(t_2^2 - t_1^2)}$$

$$= \frac{4\pi^2 \times 14.52d}{2 \times 100 \times 2.18(41.44^2 - 27.265^2)} = .001350d.$$

Multiplying the constant, .00135, by the deflection in cm., corrected as will be explained, gave the force of restitution in each case.

Determination of V.

As the volumes of the test pieces were in some cases not over .05 c.c., this operation had to be very carefully done. After trying various methods the best results were obtained by arranging two pans on an assay balance with the lower one in water at all times and the upper one in the air. These two pans were joined together by a No. 40 wire so as to lessen the action of the surface film. Two weighings were then sufficient. Their difference gave the volume.

Determination of H.

H was found in a series of positions by jerking out a test coil and cutting the lines of force. This was one of the most tedious operations in the whole experiment. Fig. 5 shows the slide used

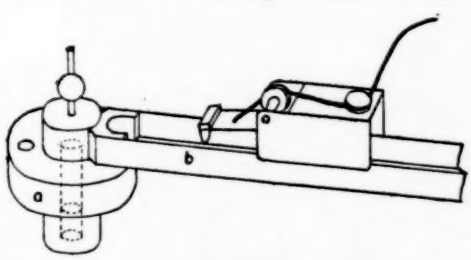


Fig. 5.

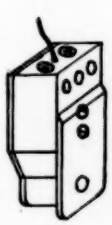


Fig. 6.

for making these tests. a was a brass block which fitted snugly into the hole of S, Fig. 1. b was an axis which fitted into a hole in

a. Attached to b was a mirror in which reflections of the circular scale gave the position and the angular movement. b was provided with a spring for holding the test coil, Fig. 6, in place. The spring could be released and the coil drawn out by suitable rubber bands.

To calibrate the exploration test coil it was connected in series with the galvanometer and another coil placed in the center of a standard solenoid, through which the current could be reversed. Then the equation giving the magnetic flux corresponding to any reading ϑ for the test coil is

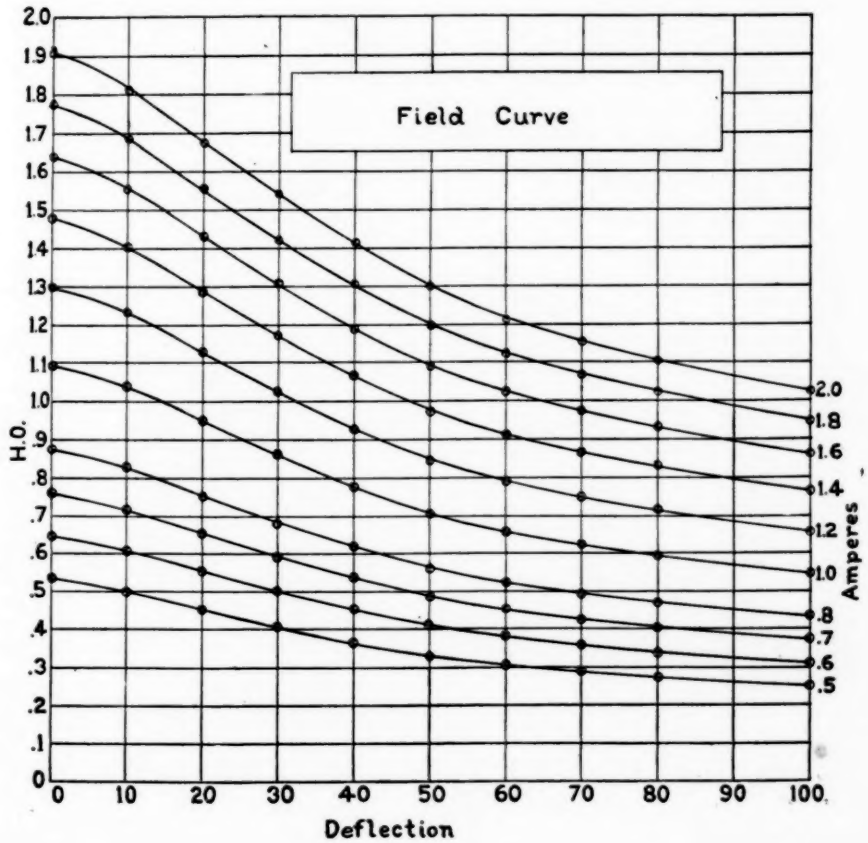
$$H = \frac{4\pi \frac{N_1}{L_1} A_1 n_1 a_1}{5na} \frac{\vartheta}{\vartheta'}$$

where N_1/L_1 are the number of turns per cm. in the standard solenoid; n_1 and a_1 are the number of turns and area of the standard coil placed in the solenoid; n and a are the same for the snatch coil and ϑ' is the deflection caused by the reversal of a current of A_1 amperes in the solenoid. The values of these constants were $N_1/L_1 = 47.3$, $n_1 = 41$ and $n = 63$ turns, $\vartheta' = 3.28$ cm., $A_1 = .07$ ampere, $a_1 = 66.4$ and $a = .203$ square cm. Substiuting these values,

$$H = 540\vartheta.$$

The test coil was pushed into b, Fig. 5, and held by the spring. The galvanometer was on another pier so as not to be jarred. The observer after setting the coil went to the galvanometer telescope and by a sudden jerk released the coil and observed the deflection. The coil was again set and released. About 2,000 such observations were made in plotting the field. A series of tests was made on one pair of poles and then on the other pair. It was found that the flux was so nearly the same that there was a variation of not more than four parts in 1,500. So the accurate plotting of the field was all made at one pole. One difficulty that showed itself continually was the residual magnetism in the field-magnet. When these tests as well as the deflections of the test pieces were run, it was almost impossible to do away with all residual magnetism, so as to start from the same condition. It was found that the double knife switch worked better when reversed by hand than any other means. After

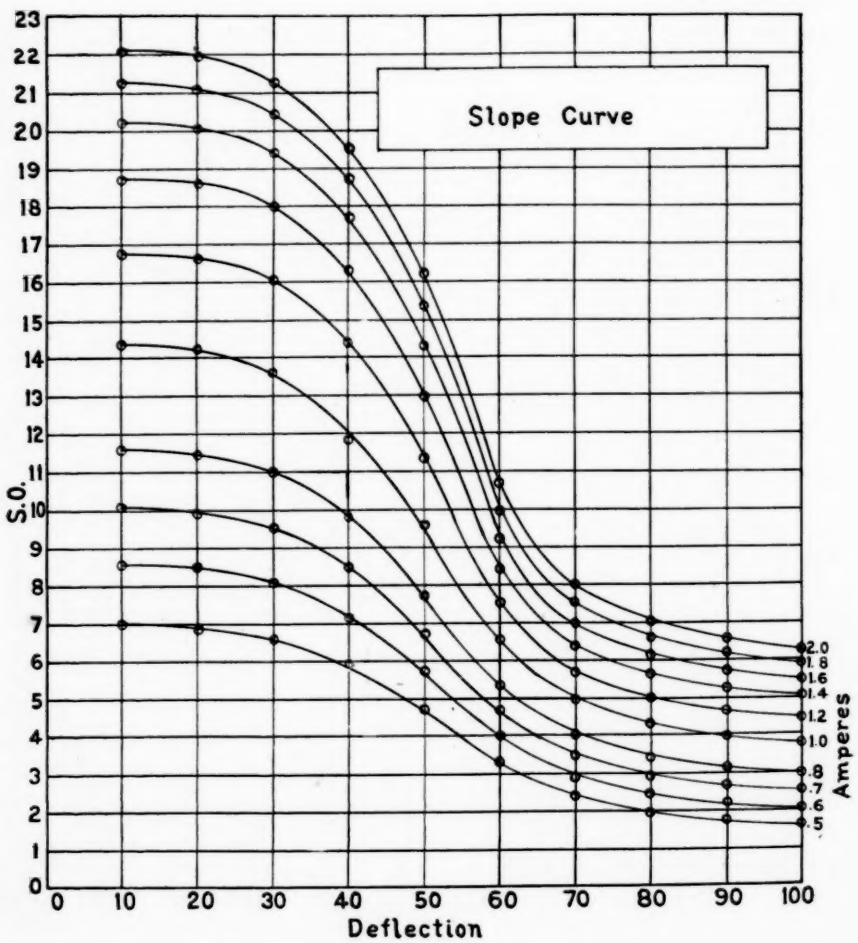
centering the field by means of a piece fitted into Fig. 5, *b* and around the pole, galvanometer deflections were observed for each tenth radian out to one radian. Here the position was fixed and the current was increased. As a check at .5, 1 and 2 amperes, the current was kept constant and the coil was moved across the field. These two sets of readings were taken to plot the field curve. By reading



off the ordinate on this curve corresponding to the current used in the magnet and the deflection of the test piece and multiplying by 540, the field strength was found. In the data this ordinate is called H.O.

DETERMINATION OF dH/dx.

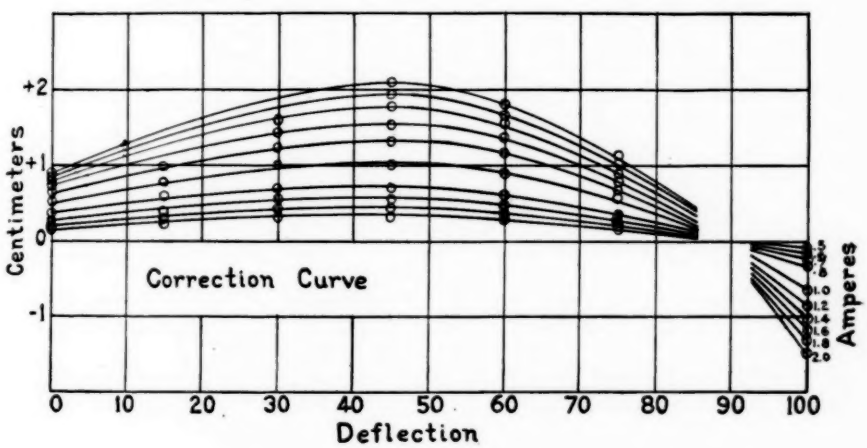
After the field curve was finished the slope at each 10 cm. deflection was found by finding the difference in ordinates in centimeters for two points 40 cm. apart on the axis of abscissas. From this data was drawn the slope curve with difference in ordinates and deflection in centimeters as ordinates and abscissas. To find the slope from this curve one found the ordinate corresponding to the current used and the deflection and multiplied by 15.38, for a motion of 40 cm. on the scale corresponded to $(2.18 \times 40/100) = 872/1{,}000$ of



one centimeter motion of the test piece and the scale of the slope curve is forty times that of the field curve. So the slope constant $= (540 \div \frac{872}{1000})/40 = 15.38$. These ordinates in the data are called S.O.

Correction Curve.

The celluloid of which the spool and spindle was made was diamagnetic as a whole, but in working or otherwise small traces of iron lodged in the material and caused a deflection of the spool alone when the field was thrown on. This made it necessary to observe the deflection from a certain position in the field for each of the fields corresponding to the currents used. From these observations a correction curve was drawn. In the spool used this cor-



rection was such as to subtract from the deflections. The deflection minus the correction, which is marked D.C. in the data, multiplied by the fiber constant, .00135, gave f, the restoring force in dynes.

Results on the Susceptibility of Bismuth.

As the method used depended upon the test pieces having their total susceptibility negative, bismuth test pieces were used to make the throw from the central position as large as possible. If the total susceptibility had been positive, they would have been drawn to the center of the field, no matter how weakly positive. The specimen to be tested was placed upon the bismuth. There was an increase

or decrease of deflection as the added specimen was diamagnetic or paramagnetic. As the whole series of experiments depended upon the accuracy with which bismuth was determined, one set of such determinations will be given.

Bismuth No. 2. March 8, 1907.

Amp.	1	2	3	4	Def.	Cor.	D.C.	f	H.O.	H.	S.O.	S.	$-\kappa \times 10^{-6}$
.0	38.6	38.6	38.6	38.6									
.5	87.8	87.8	87.8	88.0	24.62	.34	24.28	.0328	$.43^4$	237	6.79	104.2	14.0
.6	104.3	103.7	103.8	103.9	32.66	.48	32.18	.0434	$.48^8$	263	7.97	122.4	14.2
.7	115.9	116.0	116.2	116.1	38.72	.60	38.12	.0513	.544	294	8.70	133.6	13.8
.8	126.1	126.3	125.9	126.4	43.74	.75	43.04	.0580	.595	322	9.15	140.6	13.6
1.0	141.9	141.9	142.0	141.7	51.64	1.01	50.63	.0682	.698	377	9.10	140.0	13.6
1.2	153.2	153.0	152.9	153.4	57.26	1.20	56.06	.0758	.803	433	8.40	129.2	14.3
1.4	161.9	162.0	161.8	161.7	61.62	1.32	60.30	.0814	.903	488	7.90	121.6	14.6
1.6	168.9	168.8	168.7	168.7	65.09	1.36	63.73	.0860	.996	538	7.77	119.4	14.1
1.8	174.9	174.8	174.9	174.8	68.12	1.39	66.73	.0900	1.076	580	7.75	119.0	13.8
2.0	180.1	180.1	180.0	180.0	70.72	1.39	69.33	.0937	1.149	620	7.70	118.0	14.0

$V = .0946$ c.c. Mean $\kappa = -14.03 \pm .33 \times 10^{-6}$.

As will be noticed from the H. column, the field strengths where these tests were made varied from 237 to 620 lines. This test gave -14.03×10^{-6} for bismuth. Two other tests gave -13.95 and -13.82. The mean of these three is $-13.92 \pm .08$.

Van Ettenhausen[1] has made the most exhaustive study of the susceptibility of bismuth and his value found in various ways was about -14.00, though all of his values were in fields of from 2,500 to 8,000 lines instead of from 200 to 600 lines, the range of field strengths used in these determinations. Wills[2] found that for field strengths of from 1,600 to 10,000 lines the susceptibility of bismuth was approximately constant. My work would seem to show for the lower field strengths a constant value also. Wills' value was much too low compared with Van Ettenhausen's. In my preliminary tests it was found that one pair of test pieces was less diamagnetic than another pair cut from the same stick. It was noticed that the less diamagnetic was cut with a dull tool. So both specimens were boiled in hydrochloric acid to remove abrased iron and their values became the same and constant. Wills' low value may have been

[1] Pogg. Ann., clx., p. 1, 1877.
[2] Phil. Mag., 5 Series, 45, p. 446.

due to iron contamination of this sort. After it was thus discovered that the iron left on the surface by the abrasion of the tool was sufficient to influence the susceptibility of the specimen to so large a degree, all the test pieces used in these experiments were boiled in hydrochloric acid to remove this iron.

Results on the Susceptibility of Tin.

The first tin used was Kahlbaum c.p. Tests were made of this by cutting out of the square sticks in which the tin came the specimens. This tin from several lots gave about the same value for k, $+ .5$ to $+ .6 \times 10^{-6}$. One of these specimens was tested without boiling in hydrochloric acid to find the effect of the iron. This sample had a value of $+ 3.42 \times 10^{-6}$, which fell to the same as the others when thoroughly boiled in hydrochloric acid. This Kahlbaum tin which by analysis showed a trace of iron did not seem pure enough to make suitable alloys, so an effort was made to obtain the tin in a purer condition. The general method employed for obtaining pure tin was the same in all the following cases. Tin was dissolved in nitric acid forming metastannic acid, the contaminations remaining in solution as nitrates. The white precipitate was thoroughly washed with distilled water to free it of all nitrates, was dried in a steam bath and was mixed with lamp black and reduced by heating in a gas furnace. Lamp black was chosen as the reducing agent, because it seemed the form of finely divided carbon most likely to be free from iron. Three different crucibles were used in which to make this reduction, fused quartz, fused magnesium oxide and a carbon crucible made by boring out two inch electric furnace carbons and boiling in hydrochloric acid to free from all abrased iron. Specimens obtained from the three were almost exactly alike in susceptibility. So an amount sufficient for these experiments was reduced in a carbon crucible.

The susceptibility of the tin alone was found from that of the sum by taking $- 13.8$ as the susceptibility of the bismuth in the sum and solving according to relative volumes as shown. This gave the tin a susceptibility of $+ .31 \times 10^{-6}$; that is, tin was obtained which was slightly paramagnetic and not diamagnetic as Faraday[1] obtained

[1] Faraday's Exp. Researches, Series XXI., 2399.

it in 1845. It seems probable that there may be a slight iron contamination still present. This tin however seemed sufficiently pure for our purposes and was used in making the alloys.

Tin. May 6, 1907.

Amp.	1	2	3	4	Def.	Cor.	D.C.	f	H.O.	H.	S.O.	S.	$-\kappa\times10^6$
.0	38.5	38.5	38.5	38.5									
.5													
.6													
.7	89.0	89.1	88.4	88.1	25.08	.54	24.54	.0332	.624	337	9.80	150.4	3.20
.8	100.7	100.8	101.3	101.2	31.25	.71	30.54	.0413	.676	365	10.89	167.6	3.30
1.0	117.5	117.2	117.2	117.1	38.38	1.04	37.34	.0504	.791	427	12.49	192.0	3.02
1.2	129.2	129.0	128.9	128.8	45.24	1.32	43.92	.0586	.883	477	13.03	200.0	3.00
1.4	137.8	137.6	137.5	137.4	49.54	1.52	48.02	.0640	.977	527	13.18	203.0	2.95
1.6	144.6	144.2	144.0	144.0	52.85	1.66	51.19	.0683	1.068	576	12.90	198.0	2.93
1.8	149.7	149.7	149.5	149.6	55.56	1.77	53.79	.0717	1.150	620	12.47	192.0	2.95
2.0	154.4	154.4	154.2	154.5	57.95	1.86	56.09	.0750	1.225	660	11.85	182.0	3.07

Mean $\kappa = -3.05 \pm .10 \times 10^{-6}$.

Volume Sn = .1563 c.c.
" Bi = .0488 "
Total = .2051 "

$-13.8 \times 488 + 1563\kappa = -2051 \times 3.05$
$1563\kappa = 6734 - 6256 = 478$
$\kappa = +.31 \times 10^{-6}$.

RESULTS ON THE SUSCEPTIBILITY OF COPPER.

An effort to use copper chips obtained from Kahlbaum was made but this copper was entirely unusable. Even when these shavings were boiled in hydrochloric acid and melted in a boiled carbon crucible, the susceptibility was found to be $+ 9.2 \times 10^{-6}$. A sample of native copper from the Calumet and Hecla Mine was obtained. This was tested and showed itself feebly diamagnetic. This first specimen was from a small piece. Later much larger homogeneous pieces were obtained and were cut up carefully with a hack saw, filed to remove any lodged quartz and then boiled in hydrochloric acid to free the surface of iron. In this way pieces for testing and for making alloys were obtained.

Our solution gives this copper a susceptibility of $- 1.22 \times 10^{-6}$, clearly diamagnetic as Faraday[1] found it. The paramagnetism of all commercial coppers is probably due to contamination of iron acquired in remelting or tooling. Most of the native coppers con-

[1] Exp. Researches as above.

tain a little iron. Fleming and Dewar used some copper which they found from + 7 to + 28 × 10^{-6}. It appears therefore that this sample of copper is very pure and probably free of iron.

Copper. April 12, 1907.

Amp.	1	2	3	4	Def.	Cor.	D.C.	f	H.O.	H.	S.O.	S.	$-\kappa \times 10^{-6}$
.0	39.1	39.1	39.1	39.1									
.5	74.6	75.4	74.4	74.8	17.85	.29	17.56	.0237	.460	248	6.92	106.2	4.38
.6	90.2	91.8	90.7	91.5	25.98	.44	25.54	.0345	.522	282	8.32	127.6	4.68
.7	102.5	102.9	102.5	102.7	31.78	.58	31.20	.0421	.583	315	94.1	144.4	4.52
.8	111.7	112.4	111.9	112.1	36.46	.74	35.74	.0483	.641	347	10.33	158.0	4.30
1.0	126.2	127.5	126.2	127.2	43.84	1.05	42.79	.0578	.750	405	11.33	174.0	4.00
1.2	137.3	137.6	137.3	137.4	49.15	1.30	47.85	.0647	.851	460	11.70	179.6	3.82
1.4	145.5	146.0	145.7	145.9	53.34	1.51	51.83	.0700	.949	512	11.45	176.0	3.80
1.6	152.2	152.3	152.3	152.2	56.57	1.60	54.97	.0743	1.042	562	10.85	166.6	3.88
1.8	158.2	158.0	157.7	157.7	59.40	1.68	57.73	.0780	1.123	607	10.26	157.6	3.98
2.0	163.0	162.9	162.8	162.5	61.85	1.75	60.10	.0812	1.198	647	9.85	151.2	4.05

Mean $\kappa = 4.14 \pm .26 \times 10^{-6}$.

Volume Cu = .1568 c.c.
" Bi = .0488 "
Total = .2056 "

$-13.8 \times 488 + 1568\kappa = -4.14 \times 2056$
$1568\kappa = 6734 - 8512 = -1878$
$\kappa = -1.22 \times 10^{-6}$.

Results on the Susceptibility of Copper and Tin Alloys.

With the copper and tin thus prepared alloys were made by melting the copper in crucibles made from the furnace carbons boiled in hydrochloric acid and washed, and adding the tin. The smaller per cents of tin combine better and so more of the specimens were made with low value in tin. Heycock and Neville[1] have made a very exhaustive study of copper and tin alloys and an effort was made to make the alloys they considered atomic combinations. Seven alloys were prepared and their susceptibilities determined. Some of them were soft enough to be turned up. Others had to be ground. All were treated with hydrochloric acid before testing. As an example of such a test take specimen No. 5.

The other samples were tested in the same way. The per cent. of copper and tin by mass was found by analysis, because the samples were not all of them homogeneous and some of them had an excess of tin floating on the alloyed part. The per cents by mass

[1] Phil. Trans. of Royal Society, 202 *A*.

were changed to per cents by volume, as susceptibility is a function of volume and not of mass.

Cu-Sn Alloy No. 5. May 13, 1907.

Amp.	1	2	3	4	Def.	Cor.	D.C.	f	H.O.	H.	S.O.	S.	$-\kappa\times10^{6}$
.0	38.0	38.0	38.0	38.0									
.5													
.6	85.0	85.4	85.7	85.8	23.79	.43	23.36	.0315	.533	288	8.40	129.0	7.50
.7	98.2	99.4	98.9	98.8	30.40	.58	29.82	.0403	.591	319	9.51	146.0	7.66
.8	108.3	108.7	108.8	108.8	35.33	.73	34.60	.0467	.649	350	10.47	160.6	7.34
1.0	124.4	123.9	123.8	123.8	42.99	1.06	41.93	.0567	.756	408	11.52	176.5	6.96
1.2	135.1	135.1	135.0	135.2	48.55	1.30	47.25	.0638	.855	462	11.90	182.6	6.68
1.4	143.6	143.4	143.8	143.9	52.84	1.48	51.36	.0694	.952	513	11.70	179.8	6.68
1.6	150.3	150.1	150.2	150.2	56.10	1.61	54.49	.0736	1.045	563	11.10	170.0	6.78
1.8	155.9	155.8	155.7	155.9	58.91	1.70	57.21	.0772	1.126	608	10.50	161.6	6.97
2.0	160.6	160.7	160.7	160.6	61.33	1.77	59.56	.0803	1.201	649	10.05	152.0	7.20

Mean $\kappa = -7.11 \pm .30 \times 10^{-6}$.

Volume Alloy = .0646 c.c.
" Bi = .0488 "
Total = .1134 "

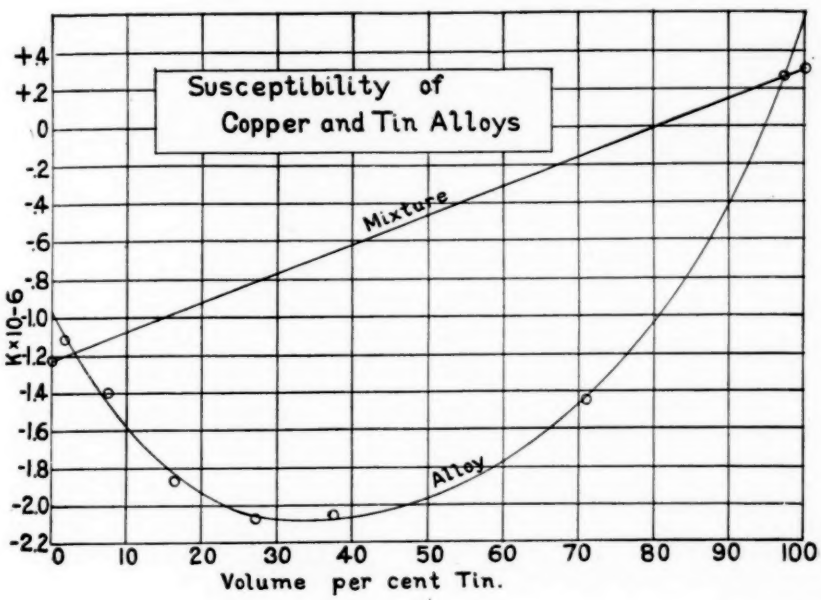
$$-13.8 \times 488 + 646\kappa = -7.11 \times 1134$$
$$646\,\kappa = 6734 - 8063 = -1329$$
$$\kappa = -2.06 \times 10^{-6}.$$

Alloy Results.

No.	Mass % Sn.	Mass % Cu.	$\frac{M\%}{D} = V_{Sn.}$	$\frac{M\%}{D} = V_{Cu.}$	Vol. Sum.	Vol. % Sn.	$\kappa\times10^{-6}$
1	1.0	99.0	.14	11.16	11.30	1.22	− 1.13
2	7.0	93.0	.96	10.45	11.41	8.41	− 1.40
3	13.8	86.2	1.89	9.68	11.57	16.36	− 1.88
4	24.2	75.8	3.32	8.51	11.83	28.00	− 2.07
5	33.2	66.8	4.55	7.50	12.05	37.8	− 2.06
6	66.4	33.6	9.10	3.77	12.87	70.7	− 1.43
7	97.9	2.1	13.40	.24	13.64	98.0	+ .28

The line marked "alloys" on the alloy curve is plotted from the data. The line marked "mixtures" gives the susceptibility on the assumption that this is a function of the per cents by volume. It will be noticed that when the alloys are formed there results a marked increase in their diamagnetism over that of the mixtures. The maximum value on this curve seems to be at about the alloy called speculum metal. Speculum metal is given by Heycock and Neville as one of the atomic compounds of copper and tin. An attempt was made to see whether the resulting susceptibility was

due to per cents of this compound dissolved in an excess of copper or tin. There seemed to be no connection. Probably all three copper and tin compounds are present and influence the results. It will be noticed from the curve that even with these carefully prepared crucibles there was some contamination and change in the susceptibility of both the copper and the tin by remelting.



Heusler[1] has found that a mixture of tin and manganese form an alloy which is much stronger paramagnetically than the manganese alone. The question presents itself, whether the tin increases the diamagnetism of the copper in the same way. Sufficient work has not been done to justify any assumption as to the cause; but all guesses applied to Heusler's alloy seem applicable. These guesses reduce to assuming that some molecular combination has taken place between the metals in the alloy, so that the new compound has new properties, among these new properties a new susceptibility.

The limitations of the apparatus were such that the tests were carried on in a very small range of magnetic field. By designing a

[1] Verhandlung der Phys. Gesell., 5, p. 219, 1903.

special magnet, the range can be much increased and the whole apparatus be made much more sensitive. The experimenter has in mind the making of special apparatus and further work among the diamagnetic metals, with a view to seeing whether some of them may not be made strongly diamagnetic by alloying as manganese is made strongly paramagnetic.

SUMMARY OF RESULTS.

1. The susceptibility of bismuth as previously found for large field strengths is shown to hold for comparatively low fields.

2. The absolute susceptibility $+ .31 \times 10^{-6}$ found for a comparatively pure sample of tin.

3. The absolute susceptibility $- 1.22 \times 10^{-6}$ found for a sample of native copper, probably free from iron.

4. The susceptibility of the alloys of copper and tin found to be a function which is not linear but increases with increasing per cent. of tin to a maximum and then decreases.

My thanks are due especially to Professor Michelson who set the problem and who has given valuable suggestions along the way, and also to the other members of the Laboratory Staff who have at all times freely given their encouragement.

RYERSON LABORATORY,
May 31, 1907.

GENERAL LAW FOR VAPOR PRESSURES. PART III. VAPOR PRESSURE OF CO_2.

By Sanford A. Moss.

THE general law for vapor pressures discussed in the previous articles[1] is here applied to observations of vapor pressure of solid and liquid CO_2 due to John Zeleny and Anthony Zeleny[2] and to John Zeleny and Roy H. Smith.[3] Remarkable agreement is found, both for solid and liquid vapor pressures. On the basis of such result, and by use of the Roche law given by Regnault as "Formula K" for water-vapor pressure, saturation-pressure equations are deduced. These represent the observations with reasonable accuracy throughout entire observed range for pressures of from about 1 mm. of mercury for vapor of solid, through the triple point, to critical pressure of 55,000 mm.

In the previous articles it is shown that the absolute saturation temperatures T_a and T_b for two given substances at the same vapor pressure, are connected by the relation

$$\frac{1}{T_b} = c\frac{1}{T_a} + k \qquad (1)$$

where c and k are constants for each pair of substances, for all vapor pressures. It was stated that the law includes a votalizing solid as well as a vaporizing liquid. The present article gives a good example of this.

The law is an empirical one, but it so well represents experiments on varied substances through a wide range that discovery of the rational law in the matter can only result in addition of very small corrections.

We may take the substance a of equation (1) as water vapor,

[1] Physical Review, Vol. 16, 1903, p. 356; Vol. 25, 1907, p. 453.
[2] Physical Review, Vol. 23, 1906, p. 308.
[3] Physical Review, Vol. 24, 1907, p. 42.

whose saturation temperatures are known. Then we have $1/T_a$ as a known function of the vapor pressure corresponding to the saturation temperature T_b for the substance b, since it is given by the temperature of water vapor for that pressure. By using this function $1/T_a$ of the vapor pressure of the substance b, and the function $1/T_b$ of the saturation temperature T_b, instead of the actual vapor pressure and saturation temperature, the curve between the two becomes a straight line. That is to say, the ordinates and abscissæ of the usual vapor-pressure curve are so transformed that it becomes a straight line.

Instead of finding values of $1/T_a$ corresponding to various pressures from a table of water-vapor pressures, we may compute them by a formula. It is shown in the last article that Regnault's "Formula K" (of a form originally due to Roche) gives values for water-vapor pressure which coincide well with the averages of values due to various observers. The values do not coincide exactly with those of Regnault or any one other observer, but do coincide as closely as do the values of various observers. In the preceding article is given the expression for water-vapor pressure (exactly equivalent to the original "Formula K").

$$\log_{10} p = 45.8372 - 1/(0.0264052 - 1.16589/T)$$

Here p is vapor pressure in millimeters of mercury and T is absolute centigrade saturation temperature. It follows that the value of $1/T_a$ corresponding to a given water-vapor pressure p is a linear function of $1/(45.8372 - \log_{10} p)$. As stated, this is by virtue of use of Regnault's "Formula K" for values of water-vapor pressure. From this and the general law for vapor pressures (1), it follows that $1/T_b$ is a linear function of $1/(45.8372 - \log_{10} p)$ where T_b is absolute centigrade saturation temperature and p is corresponding vapor pressure in millimeters of mercury for any substance. As previously expressed, by using $1/T$ instead of T and $1/(45.8372 - \log p)$ instead of p, the vapor-pressure curve is made into a straight line.

CO_2 Vapor Pressure Observations.

The observations of vapor pressure of CO_2 alluded to are probably the most complete set of which there is published record. They

cover vapor pressure of solid from about 1 mm. of mercury pressure at 140° absolute centigrade temperature, to the triple point at about 218° Abs.; as well as vapor pressure of liquid from supercooled state at about 207° Abs., through the triple point, almost to 0° C., and about 26,000 mm. pressure. The observations agree very closely with those of other accurate observers. So far as the writer knows, they are the only published set of observations making a distinction between curve for liquid and curve for solid vapor pressure, and showing the proper type of discontinuous intersection at the triple point. It is common to assume in this and other cases, that solid and liquid vapor pressures lie on the same smooth curve. This is probably never true however.

The papers cited cover two series of observations. The later and most accurate series covers the entire range above given. The earlier series covers only a portion of the range for solid only and agrees well with the later series. It was published as "Temperatures of CO_2 Snow at Different Pressures." This is of course equivalent to vapor pressure of solid CO_2. Many of the observations of the latter series are for mixtures of CO_2 snow with ether and alcohol, which the experiments show to give values identical with the CO_2 alone when stationary conditions are reached. This is as it should be since vapor pressures of ether and alcohol are negligible compared with those of CO_2 at the same temperature. The observed vapor pressure of such a mixture is probably the sum of the vapor pressures of the two constituents. A glance at a curve sheet containing vapor pressures of CO_2, ether, and alcohol on the same scale, such as the general curve in the first of the preceding articles [1] shows the insignificant values of vapor pressures of latter substances. For instance, at the critical temperature of CO_2, 31° C., where the vapor pressure is 55,000 mm. Hg, the vapor pressure of ether is about 600 mm. Hg and of alcohol is about 80 mm. Hg. The differences are more marked at lower temperatures which are the present concern. At the triple point of CO_2, 218° Abs. C., where the vapor pressure is about 4,000 mm. Hg, the vapor pressure of ether is about 7 mm. Hg, and of alcohol some unknown amount very much less. At the lower temperatures where the observations of

[1] PHYSICAL REVIEW, Vol. 16, 1903, p. 357.

the mixtures were taken, 156° to 196° Abs. C., the differences are much greater.

The published tables of the CO_2 vapor pressures in the articles under discussion, were smoothed by drawing an arbitrary smooth curve, and therefore were not desirable for an investigation such as the present. Professor John Zeleny very kindly furnished the writer with the original unsmoothed observations, which are wholly used in the following work. Both series of observations are used, no distinction being noticeable.

REDUCTION OF OBSERVATIONS.

The original observations of the experiments alluded to consisted of corresponding values of centigrade saturation temperature and vapor pressure as height of a column of mercury, for about 150 points for solid, liquid and supercooled liquid CO_2. For each of these points, absolute centigrade temperature, T (taking 273° Abs.

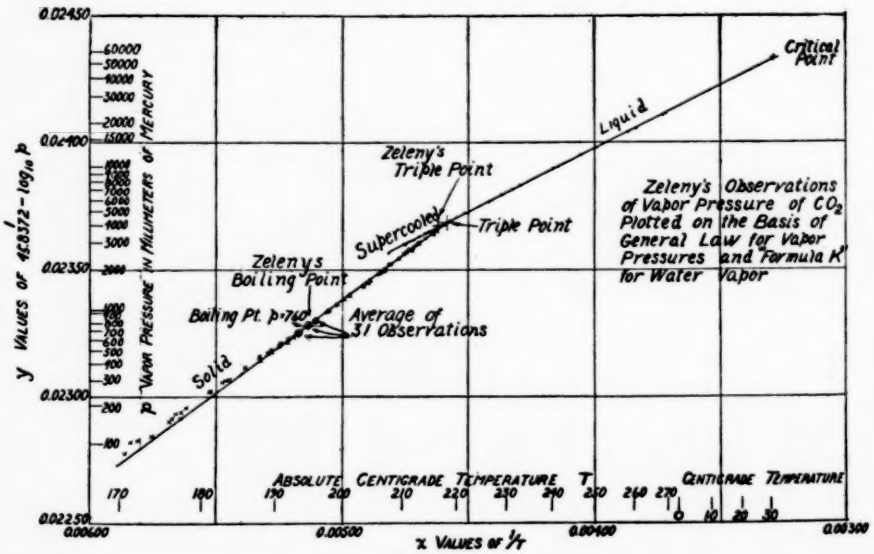

Critical Point
Liquid
Zeleny's Triple Point
Supercooled
Triple Point
Zeleny's Boiling Point
Boiling Pt. p=760
Average of 31 Observations
Solid
Zeleny's Observations of Vapor Pressure of CO2 Plotted on the Basis of General Law for Vapor Pressures and Formula K for Water Vapor
VAPOR PRESSURE IN MILLIMETERS OF MERCURY
p
y VALUES OF 1/(45.8372 − log10 p)
x VALUES OF 1/T
ABSOLUTE CENTIGRADE TEMPERATURE T
CENTIGRADE TEMPERATURE

Fig. 1.

= 0° C.), and pressure in millimeters of mercury p were computed. Thence the transformed coördinates of the vapor pressure curve $x = 1/T$ and $y = 1/(45.8372 - \log_{10} p)$ were computed and plotted on a large scale as shown by the accompanying figure re-

duced from the original. Straight lines represented the results with great accuracy. They were drawn by estimation. (In other cases which warrant the labor the method of least squares could of course be used.) Some observed points down to 146° Abs. with very low vapor pressures were given and were plotted, but are not shown on the figure. These were somewhat scattered and were given no weight. For the most part they were above the prolongation of the selected line. The observations in question did not extend to the critical point, so that this was taken as selected by Travers[1] from various observers, $T = 304°$, $p = 55{,}000$ mm. This point fell exactly on the line previously selected.

CO_2 Vapor Pressure Equations.

Two points were taken on each of the lines, solid and liquid respectively, and from them the equations of the lines were computed. For a low pressure of solid, a point on the line is $x = 0.005750$, $y = 0.022835$. The triple point is on lines of both liquid and solid and is given by the intersection as $x = 0.004583$, $y = 0.023687$. The critical point values were computed from the temperature and pressure above given, yielding $x = 0.003289$, $y = 0.024333$. These points give as the laws for liquid and solid respectively

$$0.025975 - 0.4992x = y,$$
$$0.027033 - 0.7300x = y.$$

Hence the relations between absolute centigrade saturation temperature T and vapor pressure in millimeters of mercury p for liquid and solid CO_2, are respectively

$$\begin{aligned} \log_{10} p &= 45.8372 - 1/(0.025975 - 0.4992/T), \\ \log_{10} p &= 45.8372 - 1/(0.027033 - 0.7300/T). \end{aligned} \qquad (2)$$

A few computed values are given in the table below.

It is to be remarked that in computing values of p from these equations, or in fact in any of the processes under discussion, that great accuracy is necessary in the arithmetical work, on account of the very great rapidity of variation of p. This is not the case however, for values of T.

[1] Study of Gases, pp. 245 and 247.

ACCURACY OF VAPOR PRESSURE EQUATIONS.

The following table gives a few values computed from the above equations, of course equivalent to values given by the straight lines of the figure. There are also given for comparison figures from the smoothed table of the original paper, headed "Z. and S.," as well as some of the values of Kuenen and Robson[1] and Du Bois and Wills[2] cited in the same paper. In comparisons such as this it must be remembered that very slight differences of temperature make marked differences of pressure particularly with the lower pressures.

CO_2 VAPOR PRESSURE.

Centigrade Temp.		Pressure, mm. of Mercury.			Remarks.
	Abs.	Computed from eq. (2).	Smoothed Values from Observations.		
			Z. & S.	D. B. & W. and K. & R.	
−150	123	0.028	—	—	Solid.
−134	139	0.85	1.0	—	"
−130	143	1.70	2.5	—	"
−124	149	4.53	8.0	5.0	"
−112	161	24.5	34.0	40.0	"
−102	171	80.6	99.0	110	"
− 85	188	437	435	510	"
− 80	193	671	657	—	"
− 78.5	194.5	760	—	—	Normal boiling point.
− 70	203	1,472	1,440	1,430	Solid.
− 60	213	2,961	2,980	3,020	"
− 54.8	218.2	4,169	—	—	Triple point.
− 65.5	207.5	2,562	2,508	—	Supercooled liquid.
− 60	213	3,311	3,306	3,270	"
− 58	215	3,610	3,610	—	"
− 56	217	3,952	3,945	—	"
− 50	223	5,096	5,115	5,020	Liquid.
− 40	233	7,530	7,510	7,460	"
− 30	243	10,740	10,800	10,600	"
− 20	253	14,810	14,830	14,700	"
− 10	263	20,130	19,630	19,800	"
− 7	266	21,880	21,130	—	"
0	273	26,450	—	—	"
10	283	34,170	—	—	"
20	293	43,060	—	—	"
31	304	55,000	—	—	Critical point.

[1] Phil. Mag. (6), 3, p. 149.

[2] Beibl. zu den Ann. der Physik, 24, p. 428.

Inspection of this table and of the points of the figure, shows very close coincidence between smoothed observations and values from equation, except for low pressures of the solid, below about 100 mm. Hg, and for pressures of solid immediately adjacent to and at the triple point. The latter point is discussed later. For low pressures of solid, the equation gives lower pressures than the smooth values selected by Zeleny. However, the observed points are somewhat discordant, so that possibly the smoothed values are not the true ones. Either the general law for vapor pressures fails for low pressures of solid, yielding values which are lower than the true ones; or else the difficulty of the observations for low pressures of solid makes them so discordant that it is not possible to select the true values from them. It does not seem possible to reach a positive statement in this matter from present data.

For all pressures of solid above about 100 mm. Hg (except solid pressures close to triple point alluded to later), and for all pressures of supercooled liquid and liquid up to critical point, the equations represent the observations as accurately as is possible with any smooth curve. The smooth curves selected by Zeleny from a plot of direct observations of pressure and temperature, interlace with the curves of the equations, being slightly lower or higher irregularly. In any smoothing of observations there is always some uncertainty, and the smooth values given by the equations are probably as reputable as any other selection.

The fact that the equations represent the observations with such accuracy, that is, the fact that straight lines represent the reduced observations, as shown by the figure, gives a remarkable confirmation of the vapor-pressure laws under discussion. As already stated the coincidence is so close that the empirical laws given must certainly be very close to the unknown exact laws. If a rational law is ever discovered it can only make small corrections in the values given by the empirical laws.

Triple Point.

The intersection of the straight lines for liquid and solid fixes a mathematical value for the triple point, $T = 218.2°$ Abs. and $p = 4{,}169$ mm. Hg. The observed value lies somewhat lower, but

exactly on the curve for supercooled liquid, being at $T = 216.6°$ Abs. and $p = 3{,}911$ mm. Hg. There is a sudden change in the observed curve for vapor pressure of solid, just below the triple point. The curvature changes rapidly so that the observed vapor-pressure curve seems to bend sharply upward. In the figure it leaves the straight line previously representing the reduced observations, so as to meet the line for liquid at a lower point than the intersection with the prolongation of the straight line for the solid.

Professor Zeleny has suggested to the writer that in this region just prior to melting, "the crystals or other molecular aggregates of the CO_2 gradually break up, the vapor pressure being affected by such a change."

It is to be remarked that the triple point is not the mere "melting point," but the lower extremity of the curve giving melting temperatures for various pressures. Possibly the determination of the point of intersection of this curve with the saturation curves would be of interest in the matter. The observed triple point here alluded to was found by increasing temperature of solid CO_2 exposed to its own vapor, until a point was reached where further addition of heat caused no change of temperature. Does this necessarily give a definite triple point independent of local circumstances?

It may be mentioned that the method of this paper could be applied to observations of vapor pressure of water and acetic acid published in 1884, by Ramsay and Young.[1]

The chart of the first one of these articles[2] gave a line for CO_2 vapor-pressure from Cailletet's observations as reported by Travers.[3]

These seem to be affected by the assumption that solid and liquid vapor-pressure curves are continuous, or else it was unknown that the lower observations are for the solid state. The line given should be replaced by the ones of the present figure.

Note on Parts I. and II. — As remarked in the second of the preceding articles,[4] the tables of vapor pressure given in Professor Travers' classical work "Study of Gases," are smoothed by use of a non-symmetrical form of temperature ratio law differing from the

[1] Phil. Trans., Vol. 175, 1884, pp. 37 and 461.
[2] PHYSICAL REVIEW, Vol. 16, 1903, p. 357.
[3] Study of Gases, p. 245.
[4] PHYSICAL REVIEW, Vol. 25, 1907, p. 456.

form used by the writer. Hence these tables differ slightly from results which would have been obtained from the symmetrical form of the law. This explains the fact, noted in the first of the preceding articles,[1] and not understood at the time, that the points from the tables of "Study of Gases" did not quite lay on straight lines in the large chart of the first article. Such lines therefore may differ slightly from positions exactly corresponding to original observations.

Erratum, Vol. 16, 1903, p. 358, line 5 from bottom: $-1/T$ should be $-1/T_{ic}$.

WEST LYNN, MASS.

[1] PHYSICAL REVIEW, Vol. 16, 1903, p. 360.

THE INFLUENCE OF HUMIDITY UPON THE ELECTRICAL DISCHARGE FROM POINTS IN AIR.

BY JOHN ZELENY.

THE electrical discharge from points in air is affected by the amount of water vapor present. It is of some importance to establish the magnitude of this effect so that the results of experiments performed on different days in the open air may be directly compared, and so that laboratory results for dry air may be applied to such cases, for example, as the discharge from the points of lightning conductors or the discharge from high potential wires.

Tamm[1] experimented on the current flowing from a point in air of various degrees of humidity, but unfortunately his values are given in arbitrary units and were obtained with a single potential of 6,000 volts throughout the series. The results are not suited for reducing observations from one humidity to another because the ratio of the currents for any two humidities may depend upon the magnitude of the currents in question, and upon how the humidity affects the potential required to start a discharge.

The experiments to be described in this paper had for their object the determination of the influence of humidity upon both the voltage required to start a discharge, and the magnitude of the potentials required to produce different currents.

The arrangement of the apparatus was essentially the same as that which was used in some previous experiments on point discharge, and is described on page 306 of Volume XXV. of the PHYSICAL REVIEW. A brass wire 0.26 mm. in diameter and 4 cm. long was used for the discharge point, and its rounded end was placed at a distance of 1.5 cm. from a brass disc 7.5 cm. in diameter. These were enclosed in a brass cylindrical vessel 15 cm. high and 13 cm. in diameter. The disc was connected to earth through a galva-

[1] E. Tamm, Ann. der Physik, 6, p. 274, 1901.

nometer and a telephone, while the point could be maintained at any desired potential by means of a small Wimshurst machine.

Air was drawn at a uniform rate through the enclosing vessel during each experiment, while the starting potential and the currents for a series of voltages were observed. Fairly dry air was obtained by passing the air of the room through a large calcium chloride tower; moist air was obtained by bubbling air first through hot water and then through water at the room temperature; and air of intermediate degrees of humidity was obtained by using the air of the room directly or after it had passed within different distances from water contained in bottles.

After going through the vessel containing the point and plane, the air passed through two U-tubes containing fresh calcium chloride, and then through a calibrated gasmeter. The water contents of the volume of air measured by the gasmeter was thus obtained from the increased weights of the calcium chloride tubes.

Over twenty experiments were carried out for both the positive and the negative discharges in air of different humidities. The results were all reduced to a common pressure of 74 cm. and a common temperature of 22° C. by the method given in a previous paper,[1] and the currents corresponding to the different potentials were then plotted for each case. From these potential-current curves, the values of the potentials were then read which were required to produce certain fixed currents with the air at the different humidities which had been used. Finally, the values thus obtained were plotted to show graphically how the potential required to start a current and that required to produce the currents stated, varies with the humidity of the air.

Fig. 1 represents these curves for the positive discharge. The ordinates give the potentials required to produce the currents stated, while the abscissæ are expressed in terms of the number of grams of water contained in a cubic meter of air. The abscissæ are expressed in the units given because it has been found that the changes in the point discharge in air which are produced by the addition of water vapor are related to the absolute water content of the air, and not to its relative humidity.

[1] J. Zeleny, PHYS. REV., XXV., pp. 326–331, 1907.

Evidence on this point was first obtained from the readings taken at the different temperatures on different days, but a more thorough test was made by reducing the temperature of the room to 3° C. and taking sets of readings for both discharges, first with the air dry

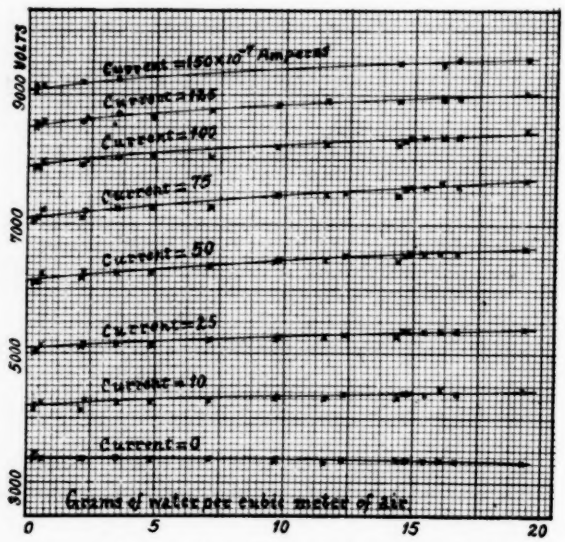


Fig. 1. The influence of humidity upon the positive discharge in air.

and then with the air saturated with water vapor. At this low temperature the saturated air contained only about one third as much water as was present in the saturated air used in the other experiments where the temperature averaged about 22° C.

The results showed that the ratio of the potential required to maintain a given current in saturated air to that required for dry air was much smaller when the air was at this low temperature than when it was at the ordinary room temperature. Moreover this ratio for the cold air corresponded in both discharges to that obtained for warm air of an equal water content, showing that the effect under consideration is dependent upon the absolute amount of water present in the air rather than upon its relative humidity.

As far as any influence of water vapor upon the ions of the air is concerned here, the result might have been expected, for although it has been shown[1] that the presence of water vapor does change

[1] J. Zeleny, Lond. Phil. Trans., 195, p. 231, 1900.

ionic velocities, still this action cannot be related to ordinary condensation at the dew point for C. T. R. Wilson[1] found that drops do not form upon the ions until the air is supersaturated over fourfold.

The points in Fig. 1 which are marked by circles are those where a faint sound was heard in the telephone indicating that the current was intermittent, at least in part. The readings were discontinued when the sound in the telephone became loud, as it usually did for high values of the current.

The curve for current = 0 in Fig. 1 represents the potentials required to start the current in the different cases. It is seen that the amount of water vapor present has but little effect upon this quantity, although the potential appears to diminish slightly as the amount of water vapor increases, the total change being about one and one half per cent. for the whole range.

The potential required to maintain a given current (between 10^{-6} and 15×10^{-6} amperes) increases with the humidity of the air, as is indicated by the upper curves of the figure. The increase is somewhat more rapid for the drier air, it is relatively not much different for the currents given, and the total change in potential for the whole range from dry to moist air is about seven per cent. in each case.

The ratio of the potentials required to produce a given current in air containing two different amounts of water vapor may be obtained readily from the curves in the figure, and used to reduce other results from the one humidity to the other.

It is desirable for some purposes to know how much the current obtained with some given potential changes with a change in the amount of water vapor in the air. This relation may be obtained by plotting the potential current curves for any two humidities in question, with values taken from the curves in Fig. 1. From these new curves the ratio of the currents for any potential is readily obtained. This ratio varies considerably from one potential to another, and for a given change of humidity is larger than the corresponding ratio of the potentials required to maintain a given current.

[1] C. T. R. Wilson, Lond. Phil. Trans., 189, p. 301, 1897.

The results of the experiments on the negative discharge are shown in Fig. 2.

As is usual, the results for the negative discharge are less regular than those for the positive discharge. It was found, however, that this irregularity diminished as the humidity of the air increased,

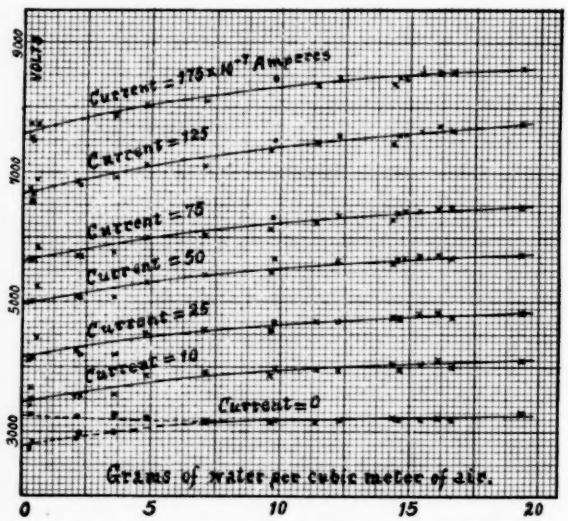


Fig. 2. The influence of humidity upon the negative discharge in air.

which indicates that moist air is to be preferred for experiments on the negative discharge.

The irregularity showed itself markedly in the retardation of the starting potential. As the potential was gradually increased when the air contained but little water vapor, the current would not increase gradually from zero value, but would start suddenly with a considerable magnitude, and it would do this in spite of the presence outside of the vessel of a tube of radium bromide which usually tends to diminish this retardation of the starting potential. It must be said that the surface of the point became coated with a rather heavy layer of oxide by its use in moist air, and it may be that this oxide in a dry state caused the large retardation of the starting potential as well as the greater irregularity of the results generally.

The curve for the starting potential, marked current = 0, is drawn in two branches for the more dry air. The upper branch represents

the average observed values, all of which are not marked. The lower branch represents values of the potentials which were obtained by extending the potential-current curves for these cases downward until they reached the axis for current = 0. Presumably these are the values of the potentials at which the current would have begun to flow had it started to flow gradually. The points on these two branches are not as concordant as would appear from the figure since some of those diverging most from the average have been omitted to avoid confusion.

As seen from the curves in Fig. 2, the potential required to produce a given current increases here also as the amount of water vapor in the air increases, the change being again more rapid when the amount of water present is small. The total increase from dry air to saturated air averages about sixteen per cent. This number does not differ greatly for the different currents used, and is much larger here than it was for the positive discharge.

The curves given may be used for reducing results on point discharge from one humidity to another in the same way as was indicated for the positive discharge.

Some experiments were carried out with alterations in what appear to be the essential experimental conditions, to determine how extended the application of the results here obtained may be. In the first of these, the distance between the point and the plate was changed from 1.5 to 3 cm., and readings were taken for both the positive and the negative discharges in air containing two widely different amounts of water vapor. In the second, similar sets of readings were taken when the point previously used (0.26 mm. in diameter) was replaced by a new one consisting of a brass wire having a diameter of 0.084 mm.

In both cases, the results for both of the discharges agreed well with those here recorded, the widest difference of about one per cent. being well within the experimental errors.

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA,
February 24, 1908.

STUDIES IN THERMO-LUMINESCENCE.

II. VARIATIONS IN THE DECAY OF PHOSPHORESCENCE IN BALMAIN'S PAINT PRODUCED BY HEATING.

BY C. A. PIERCE.

IN an earlier paper,[1] on thermo-luminescence of Sidot blende, mention was made of the interesting character of corresponding curves for Balmain's paint. These curves were obtained with the apparatus used for the study of Sidot blende. A mercury lamp was used to excite the calcium sulphide, which was in powder form. Since the lamp was made of ordinary glass and the light from it was reflected at a mirror before reaching the powder, the excitation was due to the visible spectrum in the mercury arc. Before each excitation the powder was exposed to infra-red rays in an attempt to bring it to a standard condition.

The action of infra-red rays upon the phosphorescence of calcium sulphide is not so strong as their action upon the phosphorescence of Sidot blende. In the latter case, phosphorescence due to a very long excitation can be killed off almost immediately by infra-red rays and only the highest allowable temperature, just under dull red heat, is able to produce thermo-luminescence without renewed excitation. In the case of calcium sulphide a very long exposure to infra-red rays was necessary to kill off the phosphorescence, and no exposure was found to be long enough to suppress the thermo-luminescence completely. At the beginning of the experiments on calcium sulphide this fact was not recognized. If it had been, the powder could have been brought to an approximately standard condition by heating to a temperature a little higher than the highest temperature at which thermo-luminescence was to be studied. Fortunately, in every case the powder was exposed for one minute to infra-red rays of constant strength, hence it was always brought to a semi-standard condition. No extended attempt

[1] PHYSICAL REVIEW, Vol. XXVI., No. 4, April, 1908.

was made to compare the two methods, since the blue phosphorescence of calcium sulphide is a difficult color to measure in the photometer.

The fluorescence spectrum of this sample of calcium sulphide is shown in Fig. 23. This curve was obtained by comparison with the

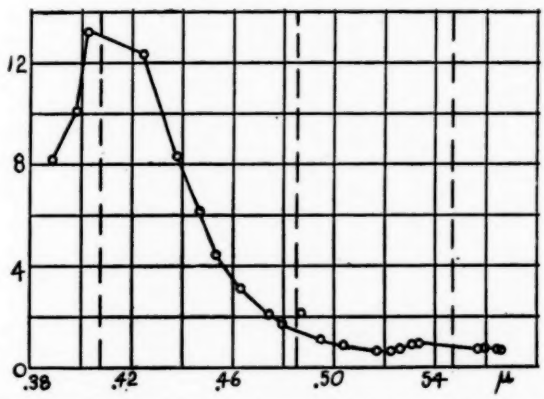


Fig. 23. Fluorescence spectrum of calcium sulphide excited by the visible spectrum of a mercury arc.

light reflected from the surface of a block of magnesium carbonate illuminated by an acetylene flame. Two bands are indicated by the curve, one with a maximum at about 0.41 μ and the other with a maximum at about 0.54 μ. The dotted vertical lines show the wave-lengths of the lines of the mercury arc. While the figure indicates a continuous spectrum this is probably due to an error caused by stray light in the spectrophotometer. The effect of this error is twofold; to lower the zero line with respect to the curve and to unduly exaggerate the ratio of the maximum of the band at 0.41 μ to the maximum of the band at 0.54 μ. Notwithstanding this correction, the band in the blue is much more intense than the other. This fact was shown by the apparent color of the initial phosphorescence, which was blue.

The effect upon the decay curve of varying the length of excitation is shown in Fig. 24. These curves are plotted with distances of the standard light from the photometer as ordinates and time measured from the end of excitation as abscissæ. For short excitations the curves are concave downward throughout, but for longer excitations

the bending is concentrated in the first part of the curves. These curves are similar to those obtained with Sidot blende, except that the phosphorescence lasts much longer. Hence it is possible to get points relatively nearer the origin. This fact allows one to make a tentative deduction regarding initial intensity and length of excitation at room temperature. A study of Fig. 24 indicates strongly that the initial intensity is greater the longer the excitation, which is the impression obtained when getting the curves. Though it is impossible, with this apparatus, to get a measurement much nearer

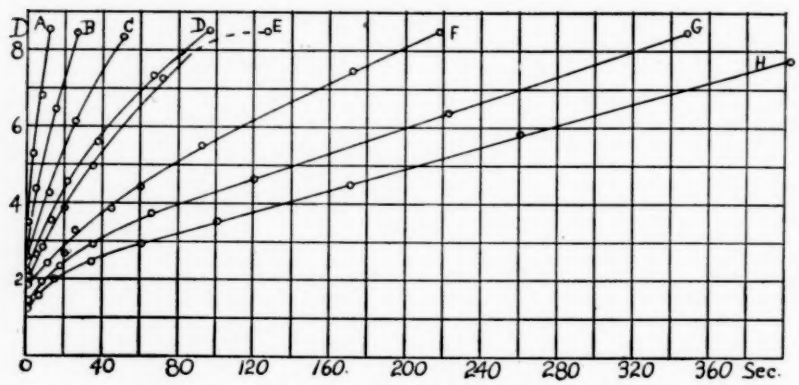


Fig. 24. Effect of varying the length of excitation. Excitation and decay at room temperature.

Curve *A*, excited	14.4 sec.	Curve *E*, excited	59.9 sec.
" *B*, "	30.1 "	" *F*, "	150.3 "
" *C*, "	30.1 "	" *G*, "	300.0 "
" *D*, "	60.2 "	" *H*, "	600.0 "

Curves *A*, *B*, *D* and *F* were taken on the second day and the remainder on the first day of the run.

the origin than 0.8 of a second, yet the eye is sensible to part of the change of intensity before this, giving one a means of estimating roughly the amount of change before the first measured point. The saturation effect is prominent as was the case with Sidot blende. Saturation is shown both by the change of initial intensity and by the change in slope of the curves as the excitation is increased.

In Fig. 24 some of the curves were obtained one day and the remainder on another day. One would expect curves *B* and *C* to coincide. The difference between them is probably due to the fact

that the infra-red exposure does not reduce the powder to a standard condition. Curves *D* and *E* agree more closely than *B* and *C*. A curve, not shown in the figure, excited for 300 seconds, coincides with *G*. This coincidence may have been due to chance, but it is what would be expected, because the effect of previous history becomes of less importance as the length of excitation is increased.

That the lack of agreement of curves *B* and *C* is due to the previous history of the powder is substantiated by the fact that curve *A* was observed immediately before curve *B*, while curve *G* was gotten immediately before curve *C*. No deductions can be made for curves *D* and *E* because the history of the powder previous to the excitation for curve *E* is not known. Curve *D* followed *B* immediately, but some preliminary work without killing off was done before killing off for curve *E*.

The changes produced in the decay curve by varying the temperature at which excitation and decay take place are shown in

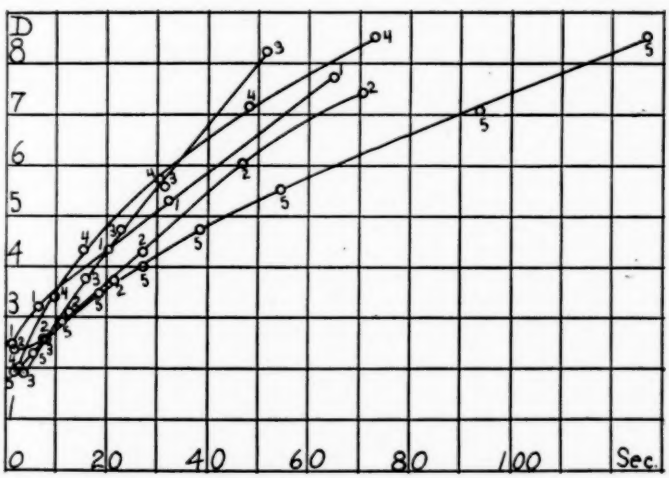


Fig. 25. Decay curves at different temperatures. Excited 2 minutes.

Curve 1. Temp. of excitation and decay, room temp.
" 2. " " " " " 66° C.
" 3. " " " " " 102°
" 4. " " " " " 145°
" 5. " " " " " 180°

Fig. 25. The part that previous history plays in these curves cannot be estimated accurately, but its effect is small because the exci-

tation, which is relatively a long one, was not changed during a set of curves. The curves were taken in the order that they are numbered. Curve 1, taken at room temperature, is similar to the typical decay curves shown in Fig. 24. As the temperature is raised the curves pass through a series of changes. Curve 2 begins concave upward but changes during the decay to concave downward. Curve 3 is practically a straight line throughout. As the temperature is raised still further, the curves again become concave downward throughout, differing not widely from the typical decay curves at room temperature.

Another set of curves similar to those in Fig. 25 is shown in Fig.

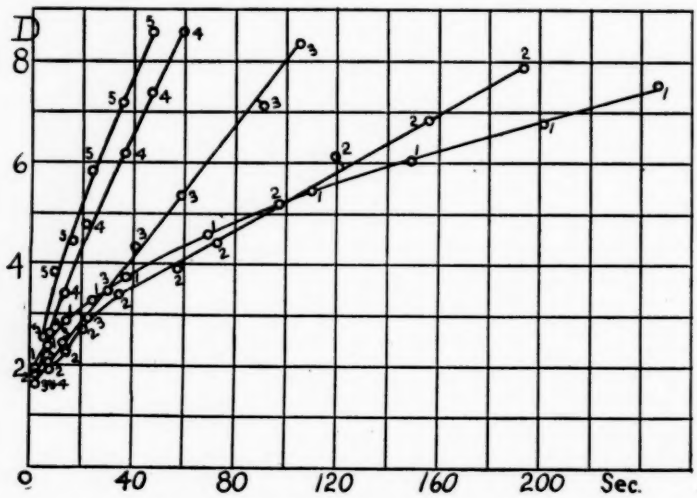


Fig. 26. Decay curves at different temperatures. Excited 10 minutes.

Curve 1. Temp. of excitation and decay, room temp.
" 2. " " " " " 42° C.
" 3. " " " " " 74°
" 4. " " " " " 101°
" 5. " " " " " 124°

26, where the length of excitation is 10 minutes. The double bending[1] is again exhibited in curve 2.

[1] When taking the runs on which Fig. 25 is based, no importance was given to the single curve which shows double bending. Later, the runs on which Fig. 26 is based were made and the apparatus was rearranged for study of another substance before the significance of the double bending was recognized. On looking over all the curves taken on Balmain's paint, other indications of double bending were found, but none of them so pronounced as those shown above. It will be necessary to repeat the runs before the existence of the double bending can be satisfactorily established.

The effect of previous history is shown in Figs. 27 and 28. These curves might readily be mistaken for curves showing the

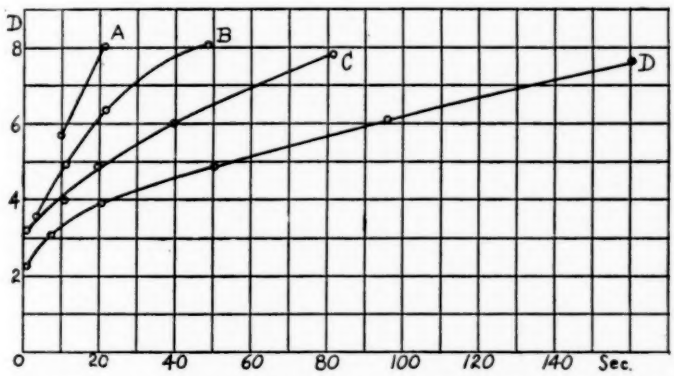


Fig. 27. Effect of history previous to excitation. Excitation and decay at room temperature. Excited 30 seconds. Curve *A*, excited after killing off with infra-red; curve *B*, excited immediately after curve *A*; curve *C*, excited immediately after curve *B*; curve *D*; before exciting for curve *D*, the powder was excited for 10 minutes and allowed to decay to an intensity corresponding to $D = 9$ in the figure, at which time the excitation of 30 seconds was begun.

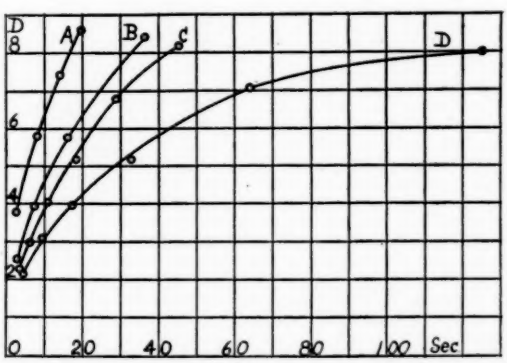


Fig. 28. Repeated curves in Fig. 27 at a temperature of 133° C.

effect of varying the length of excitation. Fig. 29 also shows the effect of previous history combined, however, with the effect of temperature.

The decay of phosphorescence in the case of Balmain's paint was studied some years ago by F. J. Micheli,[1] who has published decay curves of several phosphorescent substances, among them Balmain's paint.

[1] Arch. des Sci. Phys. et Nat., 1901, Vol. 12, p. 5.

These curves were plotted with intensity (I) and time as coördinates. For the sake of comparison, several of these curves have

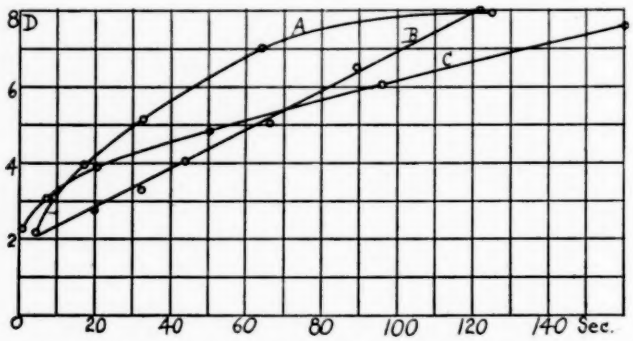


Fig. 29. Effect of history previous to excitation. Excited 30 seconds. Before each excitation, the powder was excited for 10 minutes and allowed to decay to an intensity corresponding to $D = 9$, at which time the excitation of 30 seconds was begun.

Curve C, Excitation and decay at room temp.
" B, " " " " 88° C.
" A, " " " " 133°

been replotted in Figs. 30 and 31 with $1/\sqrt{I}$ and time as coördinates. Fig. 30 shows the effect of varying the length of excitation.

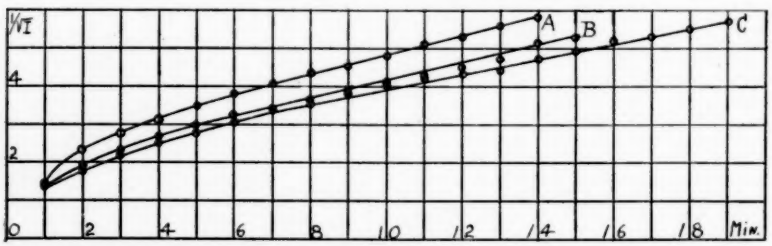


Fig. 30. Effect of varying the length of excitation. Excitation and decay at a temperature of 18° C. (Replotted from the data of Micheli.)

Curve A, excited 5 sec.
" B, " 20 "
" C, " 300 "

Another curve excited for 60 sec. coincided almost exactly with curve C.

Fig. 31 shows the effect of varying the temperature at which excitation and decay take place. These curves and the curves given earlier in this article agree generally. Fig. 31 shows the effect of excitation and decay at a temperature lower than any used in this article.

In the case of calcium sulphide, it is not necessary to use a spectrophotometer to prove that there is more than one band included in the phenomenon of phosphorescence, for under the influence of

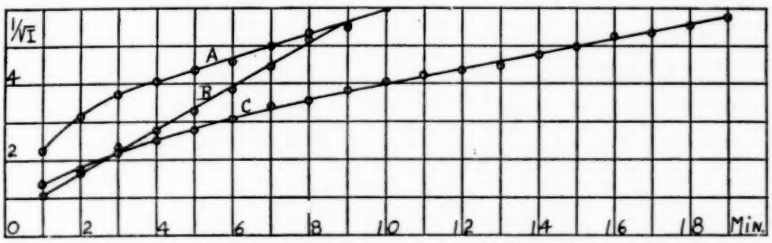


Fig. 31. Effect of varying the temperature at which excitation and decay takes place. Excited 300 seconds. (Replotted from the data of Micheli.)

Curve *A*, temp. of excitation and decay, — 21° C.
" *B*, " " " " " 100°
" *C*, " " " " " 18°

heat, the powder can be seen to change color, changing from a blue to a green. It has already been shown that the form of the phosphorescence decay curve may be closely approximated on the basis of two bands, each following the law,

$$I = \frac{1}{(a + bt)^2}.$$

This explanation was carried to some length in the author's article on Sidot blende. But there seems to be no way of combining two decays each of which follows this law so as to produce an upward bending. If it be supposed that one band increases in intensity as the other decreases, then an upward bending is possible; but a downward bending is impossible unless both the bands subsequently decay together. This suggests that one of the bands is due to some secondary effect, instead of being produced by the exciting light. Such a band would increase in intensity a certain length of time, then decrease in intensity. If we suppose that the first band follows the law suggested, and that the second band follows the same law after it has reached its maximum intensity, then the discussion given in the article on Sidot blende still holds good, the supposition being that the second band is completely formed before the first point on a curve can be measured. If, however, conditions can be changed so

that a point can be observed before the second band is completely formed, then the curve will show initially an upward bending, as in curve 2, Figs. 25 and 26. If a band is formed by some secondary effect it will usually be present in the fluorescence spectrum because the excitation is continued long enough for the band to be formed.

The effect of previous history can be explained without adding any complications to the ideas already set forth. In the case of Sidot blende, it was undoubtedly the band of longer wave-length that decayed the slower. The same is true, probably, for calcium sulphide, for the color changes from blue to green when the powder is heated. In the case of the decay curve at room temperature, the intensity is too small for the change in color to be recognized by the eye. Assuming that the band of longer wave-length decays more slowly, and that this band is due to some secondary effect, then the action of repeated excitations without intervening killing off by infra-red might be to increase the intensity and to decrease the rapidity of decay of the second band without introducing any change in the rapidity of decay of the first band. Some indications of these effects can be seen in Figs. 27 and 28.

It is unfortunate that the curves in Figs. 27 and 28 were not taken in the reverse order, *i. e.*, excitation of long duration followed by shorter excitations. Such curves, according to the ideas just set forth, should show parallelism after the decay had proceeded some time. In an article on Sidot blende by Nichols and Merritt,[1] several sets of curves were taken in this order and they exhibit parallelism after decaying a short time.

To make any attempt to explain completely the curves in Figs. 25 and 26 on the basis of a second band due to secondary causes is impracticable because the problem is complicated by the addition of the effect of temperature. One assumption will necessarily have to be added, *i. e.*, that there are certain temperatures at which either one or the other of the bands is most readily formed. This is a possible explanation of the fact that the decay curve becomes practically a straight line at one temperature.

A number of sets of curves were taken to show the effect of heating after decay has begun. For these curves the powder

[1] PHYS. REV., Vol. XXIII., No. 1, July, 1906.

was exposed to infra-red rays, then excited and allowed to decay at room temperature, heating being begun at a definite point on the decay curve. The coördinates for these curves are intensity (I) and time. Figs. 32 and 33 show the effect of varying the length of excitation. The double flash mentioned in the case of Sidot blende is plainly evident in the curves, and in the experiment was evident to the unaided eye. The color also varied, being blue for the first flash and a yellowish green for the second. At the longest excitation, the second flash is barely visible in the photometer, the only

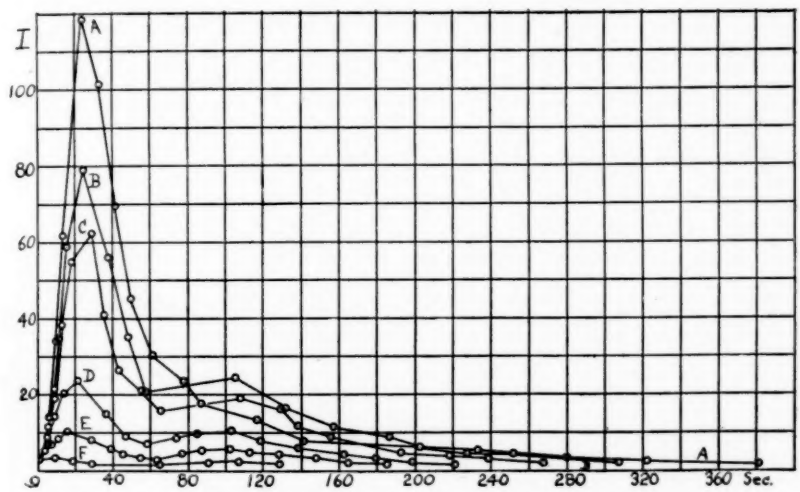


Fig. 32. Effect of varying the length of excitation. Excited and allowed to decay at room temperature to $I = 2.9$, when heating was begun. Temperature of furnace, 277° C.

Curve *A*, excited	600.2 sec.	Curve *D*, excited	60.7 sec.
" *B*, "	300.0 "	" *E*, "	30.1 "
" *C*, "	150.1 "	" *F*, "	14.8 "

evidence of its existence being a slowing up in the rate of decay. As the length of excitation is decreased, the second flash becomes, relative to the first, greater and greater.

At lower temperatures the second flash becomes less evident, and the peculiarity of the curve for 600 seconds excitation, as shown in Figs. 32 and 33, no longer exists. For the lower temperatures the second flash for 600 seconds excitation is greater than that for any shorter excitation at the same temperature. At a temperature near 100° C., the second flash is no longer evident in the curves.

It is evident that two bands are represented in the preceding curves. Any one of these curves is probably made up by the superposition of two curves, each of these component curves representing the

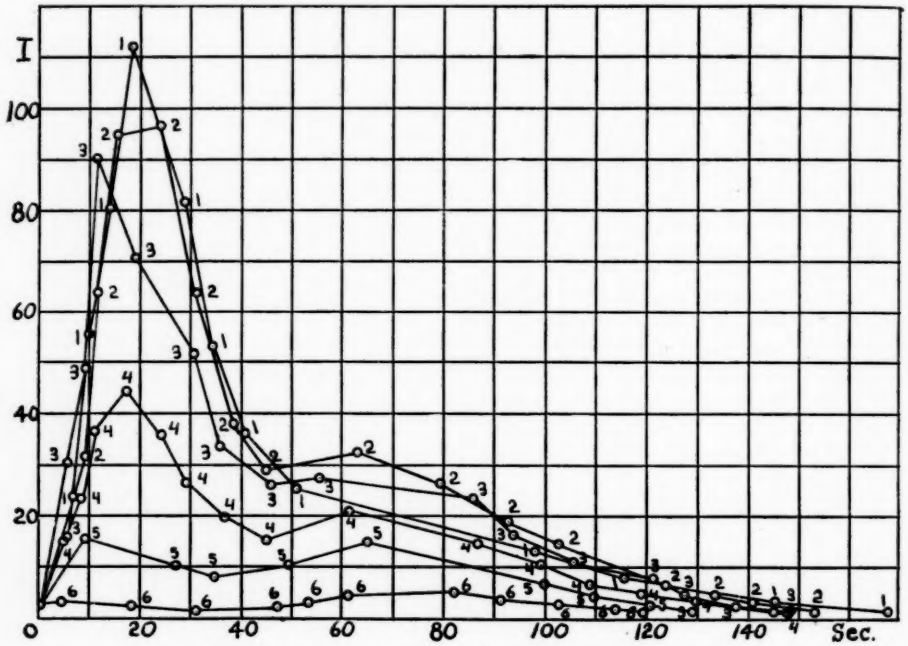


Fig. 33. Curves similar to Fig. 32. Temperature of furnace, 339° C.
Curve 1, excited 600.0 sec. Curve 4, excited 59.8 sec.
" 2, " 300.0 " " 5, " 29.8 "
" 3, " 150.1 " " 6, " 14.2 "

flash for one of the bands. If one considers the first flash in Figs. 32 and 33, it will be seen that the curves resemble closely corresponding curves shown in the article on Sidot blende. The maximum intensity increases with length of excitation and occurs later and later. The areas included between the curves and the coördinate axes increase with the excitation. The effect of saturation is shown both by the change in areas and by the change in the maximum intensities. Fig. 34 shows the maximum intensities of the first flash plotted against length of excitation.

The curves in Figs. 32 and 33 and other figures not given here can be replotted to show the effect of changing the temperature of the furnace, when the length of excitation is constant. In this case,

if one considers the first flash alone, the curves are similar to those already published for Sidot blende. Fig. 35 shows the maximum intensities of the first flash plotted against temperature.

The second flash does not always follow the laws of the first flash

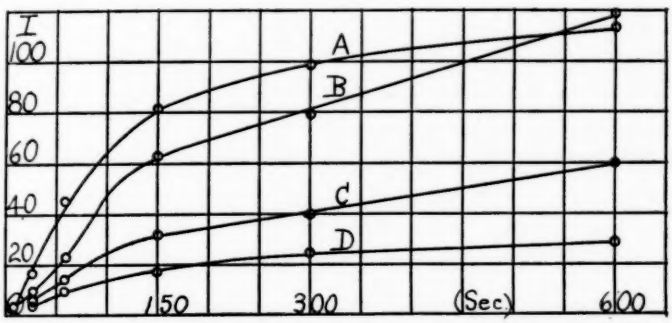


Fig. 34. Maximum intensities of the first flash plotted against length of excitation.

Curve 1, temp. of furnace 339° C. (From Fig. 33)
" 2, " " " 277° (" " 32)
" 3, " " " 222°
" 4, " " " 148°

as can be seen in Fig. 33. As the length of excitation is increased, the maximum intensity of the first flash occurs later and later, while the maximum of the second flash occurs earlier and earlier. This effect is not well defined in Fig. 32, due perhaps to the fact that the

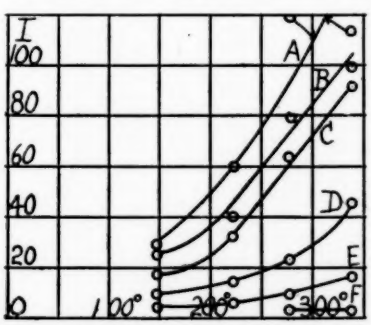


Fig. 35. Maximum intensities of the first flash plotted against temperature of the furnace.

Curve *A*, excited 600 sec.
" *B*, " 300 "
" *C*, " 150 "
" *D*, " 60 "
" *E*, " 30 "
" *F*, " 15 "

flash is of smaller intensity and consequently more difficult to follow accurately. Fig. 36 shows the effect of saturation for the second

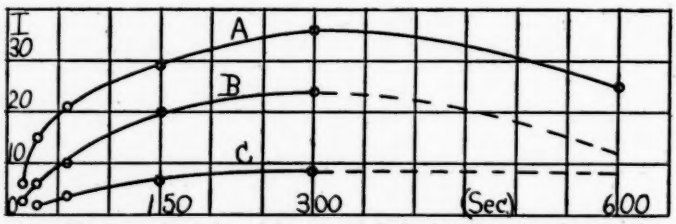


Fig. 36. Maximum intensity of the second flash plotted against length of excitation.

Curve *A*, temp. of furnace, 339° C. (From Fig. 33)
" *B*, " " " 277° (" " 32)
" *C*, " " " 222°

flash. These curves indicate that an increase in the length of excitation beyond a certain length does not increase the maximum intensity but decreases it. There is a slight possibility that the change in maximum intensity noticed for an excitation of 600 sec-

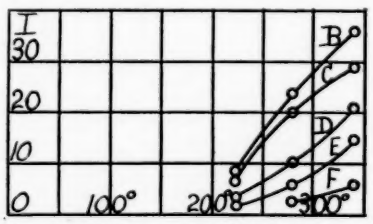


Fig. 37. Maximum intensity of the second flash plotted against temperature of the furnace.

Curve *B*, excited 300 sec.
" *C*, " 150 "
" *D*, " 60 "
" *E*, " 30 "
" *F*, " 15 "

onds may be due to previous history, the excitation of 600 seconds always being the first run of a series. In contradiction to this is the fact that a practice run almost always preceded the series. Furthermore, the peculiar change in the second flash does not exist for lower temperatures, as curve *C*, Fig. 36, and other curves, indicate.

The relation between the maximum intensity of the second flash and the temperature is shown in Fig. 37. This figure corresponds

closely to Fig. 35, which shows the corresponding relation for the first flash.

Fig. 38 shows the effect of delay in heating. Fig. 39 shows the same curves plotted with time measured from the beginning of

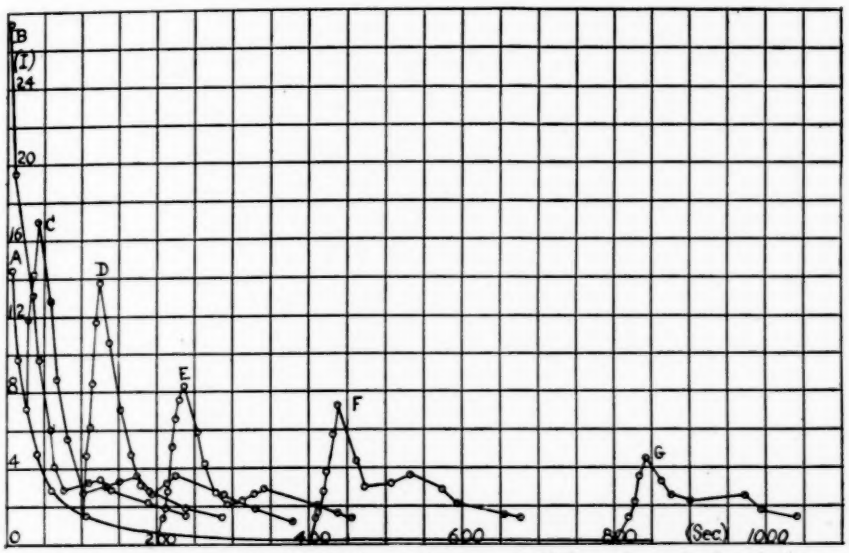


Fig. 38. Effect of delay in heating. Time measured from the end of excitation. Excited 60 seconds at room temperature. Temperature of furnace, 228° C. Curve *A*, decay at room temperature. The time between the end of excitation and the beginning of heating is as follows:

Curve *B*, 2.1 sec.	Curve *E*, 203.2 sec.
" *C*, 25.6 "	" *F*, 401.7 "
" *D*, 101.7 "	" *G*, 801.7 "

heating. Here again, if one considers the first flash alone, the curves are similar to those shown in the case of Sidot blende. The longer the delay in heating, the less intense the flash, and the later the maximum intensity of each flash. Furthermore, the time of decay for curves at one temperature and constant length of excitation is constant. It is difficult to make any deduction from the points representing the second flash.

Another set of curves similar to those shown in Fig. 38 is shown in Fig. 40. These curves show that the second flash becomes relatively larger with respect to the first as the excitation is shortened. Curve *C* shows that the second flash, under suitable conditions, may become considerably larger than the first.

It is difficult to say how much difference exists between the behavior of Sidot blende and Balmain's paint. The decay curves

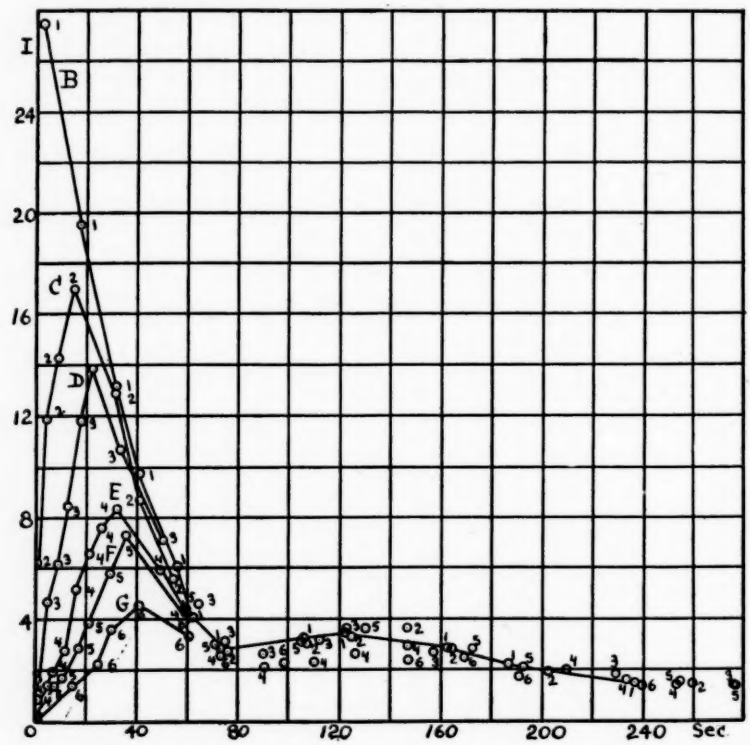


Fig. 39. Effect of delay in heating. Time measured from the beginning of heating. Same curves shown in Fig. 38.

at room temperature are very much alike. As the temperature is raised both decay curves become straight lines, but Balmain's paint shows a transition through a double curvature decay before reaching the straight line decay, while Sidot blende does not exhibit this phenomenon. Above the temperature at which the decay curve becomes straight, Balmain's paint shows a decay approximating the decay at room temperature, while in the case of Sidot blende the decay is too rapid to be followed with the available apparatus. The decay of Sidot blende is so rapid that one cannot get enough points on a curve to say positively that it does not exhibit double curvature at temperatures much higher than room. In the cases where the powder is heated after excitation, Balmain's paint shows

a double flash under some conditions, and one flash under other conditions, while Sidot blende shows one flash under all conditions,

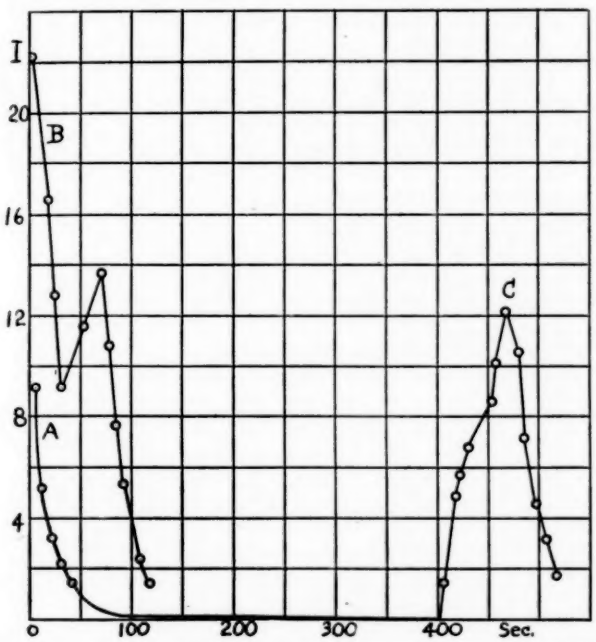


Fig. 40. Effect of delay in heating. Time measured from the end of excitation. Excited 30 seconds at room temperature. Temperature of furnace, 338° C.

Curve *A*, decay at room temp.
" *B*, waited 2 sec. after excitation before heating.
" *C*, " 400 " " " " "

unless it be admitted that there are indications of a double flash in some of the Sidot blende curves, in which case the two substances show substantially the same curves. Considering the first flash only, there is perfect agreement between the curves of Sidot blende and Balmain's paint. The action of infra-red is more marked in the case of Sidot blende, but otherwise, there is no marked difference. The fluorescence spectrum shows two bands in the case of each substance, but there is one point of difference, in that the band of shorter wave-length is more prominent in the case of Balmain's paint and less prominent in the case of Sidot blende than the band of longer wave-length.

PHYSICAL LABORATORY,
CORNELL UNIVERSITY.

(Contribution from the Cryogenic Laboratory of Wesleyan University.)

EFFECT OF MECHANICAL VIBRATION UPON CARBON DIOXIDE NEAR THE CRITICAL TEMPERATURE. II.

BY W. P. BRADLEY, A. W. BROWNE AND C. F. HALE.

IT has already been shown[1] that saturated carbon dioxide within a couple of degrees of the critical temperature is extraordinarily sensitive to minute but sudden increase of volume and thus gives rise under suitable conditions to fog effects. The fog consists of droplets temporarily suspended in the vapor phase or of gas bubbles similarly suspended in the liquid phase.

It was also shown that when the well-known Cailletet liquefaction apparatus is used such fog may be produced by mechanical vibration communicated to the mercury column from without. This may be accomplished most effectively by means of a steel rod clamped horizontally to the body of the apparatus and made to vibrate vertically. Certain quantitative relations between the frequency of vibration and the condition of the carbon dioxide were also given and discussed in the former paper.

In the present paper it is proposed to set forth certain observations which though qualitative in their nature appear to merit attention.

DYNAMIC AND RESIDUAL FOG.

If the carbon dioxide system is in a state of thermal equilibrium, sufficiently gentle vibrations produce *dynamic* fog — that is, fog which clears up at once when the vibrations are interrupted. On the contrary, if the vibrations are of greater amplitude fog often remains for a time after they cease. Such *residual* fog clears away in part by settling. The droplets of the vapor phase fall as well as evaporate, and the bubbles in the liquid phase rise as well as condense. Such droplets and bubbles as are originally large enough reach the meniscus.

[1] PHYSICAL REVIEW, *19*, 1904, 258–272.

Residual fog appears denser in transmitted light than the dynamic fog which immediately precedes it, while by reflected light the reverse is true. The theory already advanced,[1] according to which the dynamic fog is produced by intermittent expansion of the system, affords ready explanation of the first of these facts. Dynamic fog is discontinuous; it exists only in pulses. Between the pulses light has unobstructed passage.

An explanation of the action of reflected light is not so immediately apparent. Residual fog, being continuous, might be expected to reflect more light than dynamic fog, which is intermittent. However, dynamic fog doubtless consists of droplets or bubbles which are both more numerous and in part at least larger than those of residual fog. Those which are produced earlier in the fall of the mercury column would naturally, as expansion progresses, become larger than such as begin to form later. Conversely, at the return of the column they would persist longer. Residual fog could only consist therefore of such droplets or bubbles as had once been large and were now very much reduced in size. It will be understood of course that all of these, both large and small, are of microscopic size and that the terms "large" and "small" are used in a relative sense only.

An explanation is yet lacking of the fact that residual fog can exist at all under thermal equilibrium. According to the theory fog forms only during one quarter of the complete vibration — that is, during the time when the mercury column passes from its initial position of rest, which is also the equilibrium point, to the lowest limit of its oscillation. Fog is disappearing on the other hand during the next quarter of the vibration while the column approaches the equilibrium point again. As these periods are equal in length and opposite in direction the expansion of the first should be exactly offset by the compression of the second, and the condition of the carbon dioxide at the end of the second quarter should be in so far exactly the same as at the beginning. In other words there should be no residual fog under thermal equilibrium. The fact that residual fog can nevertheless be obtained, indicates a lag in the disappearance of the larger droplets and bubbles.

[1] *Loc. cit.*, page 261.

THE SENSITIVENESS OF THE SYSTEM.

The sensitiveness of the carbon dioxide to vibrations depends on two classes of factors. The first class includes such as relate to the form and construction of the Cailletet apparatus, and which may therefore be termed *external.* The second class includes such as relate to the condition of the carbon dioxide, and may therefore be called *internal.* Among the external factors affecting sensitiveness are, (*a*) the relative volume of the pressure jacket, (*b*) the thickness of its walls, and (*c*) the internal diameter of the pressure tube.

(*a*) It is obvious that if the pressure tube opens into a pressure jacket the volume of which is very large in comparison with that of the carbon dioxide, a very minute yielding of the walls of the jacket will suffice to produce a relatively large change in the volume of the carbon dioxide. In these experiments the ratio between the volume of the jacket and that of the compressed carbon dioxide varied from 1260 : 1 when the carbon dioxide was nearly all vapor, to 1760 : 1 when it was nearly all liquid.

(*b*) The thickness of the walls of the pressure jacket will largely determine to what extent those walls will yield under given circumstances. Their thickness doubtless will also determine in the main the general range of the pitch of the vibrations to which they shall easily respond. Thick walls might be expected to respond most satisfactorily to vibrations of higher frequency, and *vice versa.* To investigate such factors as the two just mentioned would require experiments with a number of pressure jackets of varying construction.

(*c*) The width of the tube in which the carbon dioxide is contained proves to be of prime importance. Experiment shows that the wider the tube the denser is the fog, other conditions being the same. This was to have been expected, since in a wide tube vibrations of given amplitude produce a greater change in the volume of a given mass of substance than is the case in a narrow one. Moreover as the change of volume produced by such vibrations varies with the square of the internal diameter of the tube the advantage gained by using a wide tube increases very rapidly with the diameter. There is a second reason of perhaps still greater importance. In a narrow tube an altogether disproportionate amount of the substance is brought under the immediate thermal influence of the walls, and

becomes quite incapable of adiabatic expansion. Indeed very narrow tubes such as are frequently used in the prosecution of critical temperature work are quite unsuited to the kind of observations here described. An internal diameter of 5 mm. is desirable, and tubes of much larger diameter may be used to great advantage.[1]

The internal factors affecting the sensitiveness of carbon dioxide include (*a*) temperature, (*b*) location of the meniscus, (*c*) vertical distance from the meniscus.

(*a*) Of these, temperature is by far the most important. When the carbon dioxide is in thermal equilibrium residual fog practically cannot be produced, in such an apparatus as we have used, at a temperature below 30° C. Above 30° the difficulty decreases at a remarkably accelerated rate. In fact at about 31.1° or 31.2°, the meniscus being still visible, it is difficult to avoid residual fog. Moreover the latter becomes singularly dense and white, reminding one in a way of hard drifted snow[2]. The duration of residual fog, once produced, goes hand in hand with the sensitiveness of the carbon dioxide to its production. At 30° it would hardly be noticed at all by one who was not looking for it, so quickly does it disappear. At 31.1° or 31.2° on the other hand it has been observed to last for 16 seconds in a phase of only 5 mm. depth. Doubtless there are at least three reasons for this. In the first place at the latter temperatures a greater amount of fog is produced, so that more time is required for the evaporation of the droplets or for the absorption of the bubbles. In the second place the texture of the fog is coarser, which also delays evaporation and condensation respectively. Thirdly, settling is much slower in close proximity to the critical temperature, for the evident reason that the densities of the two phases become so nearly alike in that region.

[1] It may be remarked in this connection that tubes of considerable internal diameter, if properly prepared and mounted, are capable of withstanding critical pressures without possessing unusual thickness of wall. Thus with the 5 mm. internal diameter and 1 mm. thickness of wall an average tube of Jena glass will withstand a pressure of 200 atmospheres before bursting. The same may be said of ordinary soft German glass though the latter is considerably more erratic in its conduct. Bradley & Browne, Journal of Physical Chemistry, *8*, 1904, 37–55.

[2] So extraordinarily sensitive indeed is the system in the immediate neighborhood of the critical temperature that one is led to the query whether the fog layers so frequently mentioned in connection with the use of the Natterer tube may not often be occasioned by the exceedingly slight changes of volume which arise from some jar to the tube as a whole.

At 31.1° to 31.2° is found the maximum sensitiveness of the carbon dioxide to the production of dynamic fog also — a sensitiveness which always greatly surpasses the other, as has been stated.

The reason is probably to be sought in part in the situation as to latent heat at that temperature. The real barrier to sudden passage from the liquid to the gaseous state or the reverse is latent heat. The smaller the latent heat the greater is the mass of substance which can be changed from one physical state to the other by the expenditure of a given amount of energy. Now the latent heat of any substance decreases very rapidly as the latter approaches the critical temperature and the barrier between the liquid and the gaseous state is correspondingly lowered. Less and less energy is thus required to transform a visible mass of substance from one state to the other.

If this were the only consideration however, the maximum of sensitiveness should be reached exactly at the critical temperature, which is not the case. From 31.2° upward the sensitiveness decreases again very rapidly, owing perhaps to the rapidly approaching equality of density and therefore of optical properties as between the droplets or bubbles on the one hand and the medium in which they are suspended, on the other.

(*b*) Even with perfect thermal equilibrium, dynamic fog is seldom of equal density in the two phases of the carbon dioxide. It may even be lacking altogether in one of them. Its location in one or the other of the phases, or the relative densities, if it is present in both phases, are found to depend partly upon the relative volumes of the phases — that is, upon the height of the meniscus — and partly on the amplitude of the vibrations.

In general when the vapor phase is subordinate in volume, or in other words when the meniscus stands high, the gentlest bowing which is effective at all produces fog in the vapor phase only. With progressively increasing amplitude of vibration this vapor fog becomes denser. Presently fog begins to invade the liquid also. All but invisibly thin at first, this fog also grows in density but always remains thinner than that in the phase above. Conversely, under the same circumstances but with decreasing amplitude, fog disappears first from the liquid and later from the vapor.

The reason for this disparity in sensitiveness is not far to seek. As the specific compressibility of the vapor phase exceeds that of the liquid a greater share of the expansion to which the system as a whole may be subjected falls to the lot of the vapor phase. This general superiority of the vapor phase in point of sensitiveness is of course greatly accentuated when its volume is least — that is, when the carbon dioxide is all but wholly in liquid form, for then a given amount of expansion bears a larger ratio to the total vapor volume.

On the other hand if the meniscus stands sufficiently low and the liquid volume is made sufficiently subordinate the whole situation is reversed. Fog appears first in the liquid phase and afterwards, with greater amplitude of vibration, in the vapor. However, a much stronger vibration is required in this case to produce any fog at all.

It would naturally follow from the foregoing that at a temperature very near the critical, where the two phases become practically identical,[1] equality of fog density should be secured when the latter are present in equal volumes. That this is only approximately true may perhaps be accounted for by the unequal influence of gravity on the two phases. The force of gravity tends to assist the formation of droplets in the vapor phase and to hinder their evaporation when formed, while it restricts the formation of bubbles in the liquid phase and assists in their recondensation. Moreover its effect on the bubbles is greater than on the droplets, because the former are subject to the weight of both liquid and vapor.

For temperatures further from the critical, but still within the egion now under discussion, a correspondingly lower position must be chosen for the meniscus, if equality in fog density is to be secured. This may be accounted for by the greater difference between the densities of the liquid and vapor phases at lower temperatures.

[1] In the use of the term "identical," it should be understood that nothing is implied as to the homogeneity of either phase near the critical temperature. Whatever difference of view may prevail as to the nature of the critical state it can doubtless be shown that if the two phases are kept in equilibrium, either mechanically by mixing, or by diffusion through sufficiently long contact with one another, they do become identical at the critical temperature. Observations which seem to indicate a difference between phases at the critical temperature can probably be explained by the fact that proper contact between the two has either been prevented or has been insufficient for the establishment of equilibrium. However in the opinion of the writers identity of the two phases at the critical temperature is perfectly consistent with heterogeneity in each.

In the phase of greater density greater inertia must be overcome locally during such rapid fluctuations of volume as are involved.

The foregoing discussion is based on observations taken at stationary temperatures[1] and during equilibrium between the two phases. That the first of these two conditions does not of necessity imply the second cannot be too strongly insisted upon.

Near the critical temperature, as is well known, small differences of temperature correspond to great differences of condition in the two phases, and the phases themselves meanwhile are so nearly alike that these differences of condition require a very considerable time for readjustment, unless the process is hastened artificially. Among the devices often employed for such a purpose may be mentioned the use of a bit of iron caused to move about within the system by means of a magnet held outside, and the practice of frequently reversing the (Natterer) tube so as to bring the phases into intimate mechanical contact with one another. These methods were impracticable in our experiments and they were also unnecessary, for it was found that strong bowing of the vibratory rod was an effective substitute. In this way, an agitation of the carbon dioxide could be induced which was veritably tempestuous, particularly so if the bow was held at a certain angle from the vertical. Equilibrium between the phases was recognized as established when gentle bowing produced a constant result after several such periods of turmoil.

Effect of Rising or Falling Temperature.

Starting at thermal equilibrium, raising the temperature of the carbon dioxide by a small amount has the effect of shifting the fog downward, either wholly or in part, out of the vapor into the liquid. Moreover the fog becomes residual and is produced by the slightest touch of the bow. That this should be so is not strange. Rise of temperature induces supersaturation in the liquid and a condition of unsaturation in the vapor. Falling temperature of course produces the opposite result, and throws the fog into the vapor which now has become supersaturated, and out of the liquid which is now unsaturated.

[1] *Loc cit.*, page 263.

The sensitiveness of the fog as a test for detecting minute changes of temperature is extraordinary. The thermostat[1] which we employed during the period of our most careful observations was capable of maintaining constancy of temperature to one thousandth of a degree Centigrade for a considerable period of time, and the Beckmann thermometer with its electrical vibrator enabled us to read temperatures to one or two thousandths of a degree. So sensitive however are these fog effects as an indication of thermal change, that variations in temperature of even this order were heralded by the fog many seconds before they became apparent otherwise.

In the study of unsaturation and supersaturation, two methods were employed for securing minute thermal changes in the carbon dioxide.

One of these consists in slightly decreasing or increasing the volume of the carbon dioxide, and so in temporarily raising or lowering its temperature by adiabatic compression or expansion. This can easily be done by slightly opening for a moment the needle valve, which closes communication between the steel pressure jacket of the Cailletet apparatus and the hydraulic pump which develops the pressure. If the pressure in the pump is made slightly greater or less than that which prevails in the Cailletet apparatus, a slight opening of the valve for a moment permits a minute amount of water to enter or to leave the pressure jacket, so as respectively to decrease or increase the volume of the carbon dioxide. In this way it was possible to change the internal temperature of the carbon dioxide suddenly in either direction, and then to watch the phenomena attending its gradual recovery. In connection with such a study some rather curious effects were observed.

If the bath temperature is very near the critical, and the height of the meniscus is such as to correspond to dynamic fog in the liquid, a very minute decrease in the volume of the carbon dioxide causes the meniscus suddenly to disappear, in consequence of the rise of temperature produced by the compression. Suitable bowing now produces very dense dynamic and residual fog in the whole region just occupied by the vapor, and none at all in that which contained the liquid. The lower limit of the fog is the disc where the

[1] Bradley and Browne, Journal of Physical Chemistry, *6*, 1902, 118–135.

meniscus formerly was, and the limit is just as sharply defined as if the meniscus were still there. Presently as the heat of compression becomes gradually dissipated, the meniscus suddenly reappears, but on a higher level, within the fog zone. Still the latter continues for a time to be bounded exactly as before, until the thermal equilibrium between the carbon dioxide and the bath is almost complete. Then, according to circumstances, there may be noticed one of two things. If the meniscus is still low enough to correspond normally to fog in the liquid only, fog presently appears in the older liquid region also and becomes rapidly denser, while that above the old position of the meniscus grows thinner. Finally, with sufficiently gentle bowing, the fog disappears entirely in the vapor phase above the new meniscus, and extends throughout the whole of the liquid from the new meniscus down to the mercury. In the other case, when the new meniscus is high enough, the fog in the region between the new and the old meniscus gradually thins until finally the fog is confined to the zone above the new meniscus. Which of these alternatives carries the day depends, as has been said, upon the height of the new meniscus — whether it normally corresponds to fog in the liquid only, if still low enough, or to fog in the vapor only, if at a higher level.

The noteworthy feature of the situation is that newly formed liquid is not allied in sensitiveness to the older liquid at all, but to what remains of the vapor phase. Clearly the new liquid is saturated like the vapor, while the old liquid for a time is not. The sharpness of the fog line between the new and old liquid appears to be due to differences of density of considerable magnitude, and not in general to any inability of the two to mix with one another, for the turmoil produced by firm bowing does mix them and throws the fog limit at once up to the new meniscus.

For the most part there was nothing whatever except the fog phenomena to indicate the boundary between the two layers of liquid. Twice an additional phenomenon occurred, namely, the existence of two visible menisci in the system at once — the new permanent one above, and a temporary one, which appeared where the old one had been, lingered a moment and then disappeared, leaving only the fog limit to mark the spot as before. Every effort

which ingenuity could suggest was employed to multiply instances of this sort, but without result. It would have been natural to conclude that both of the cases mentioned were an illusion, if it were not that each was observed by two operators simultaneously.

A sequence of phenomena which is in part the reverse of that already mentioned as attendant upon slight but sudden compression of the carbon dioxide may be established by correspondingly increasing the volume by a slight amount. In this case the meniscus naturally does not disappear, but drops suddenly to a lower level. The expansion results in the immediate appearance of dense fog in both phases. If left undisturbed, the fog becomes thinner and finally disappears, while the meniscus gradually descends to a still lower level. During this process gentle bowing thickens the fog from the bottom of the liquid up to the point from which the meniscus is gradually receding — an indication that the vapor newly formed from the liquid is both denser and more saturated than that of longer existence. The upper limit of the fog is very sharply defined. Continuation of the gentle bowing results finally in dynamic fog on only one side of the meniscus, according to the height of the latter, as previously explained. At any time in the process, firm bowing causes at once all difference in sensitiveness between the older and the newly formed vapor to disappear.

The other method of changing the temperature of the carbon dioxide is the obvious one of gradually changing the temperature of the bath. Naturally it is much more time-consuming, but on the other hand the results are simpler. In this case, the vapor phase is always unsaturated during rising temperature, and yields fog with difficulty or not at all, while the liquid is supersaturated and yields both dynamic and residual fog. When the temperature is falling the reverse is true.

As the position of the meniscus changes very gradually indeed by this method of altering the temperature, there is practically no opportunity for the study of differences of sensitiveness between new and old liquid, and between new and old vapor respectively, unless all bowing of the vibratory rod is discontinued for a considerable period of time, during which new liquid or new vapor accumulates somewhat in the absence of agitation.

The influence of strong bowing as a means of changing existing relations between the two phases has been mentioned already. A further instance may be given at this point before leaving the subject of fog zones. With the carbon dioxide at a temperature which is constant and very near the critical, and with the meniscus at about the height proper for equality of density in the dynamic fog of the two phases, sufficiently firm bowing produces a condition resembling opalescence in the whole system, attended, as before explained, by wild confusion in the region of the meniscus. If the bowing is then interrupted, the meniscus settles at once into place and the opalescence gives way to a belt of residual fog of great density, which finally disappears, partly by settling and partly by absorption. This belt extends to approximately equal distances on each side of the meniscus. The width of the belt depends on the duration of the bowing. If the firm bowing is then renewed without waiting too long, the belt gives way at once to the former opalescence of dynamic fog. Once, because of some peculiar handling of the bow no doubt, this second opalescence was succeeded by a system of six sharply defined zones, four of which consisted of residual fog. At the center was a dense belt as before, cut in two by the meniscus. On the upper and lower sides of this belt was a layer of thinner fog, and beyond this in either direction a zone of no fog at all. On every other occasion a second bowing resulted like the first in a single belt of residual fog, or in other words, a system of four zones with the meniscus in the center. The belt however was wider than before. Whatever the number of zones may be, the boundaries are in all cases absolutely sharp and horizontal, and within any given zone no shading off in density is to be observed in either direction.

(*c*) *Sensitiveness at the Meniscus.*— In a system which is in a condition of equilibrium as nearly perfect as constancy of temperature in the bath, occasional firm bowing, and time can make it, the very gentlest bowing which is capable of giving a visible result produces dynamic fog at the meniscus, without any sharpness of boundary vertically. If it is in the vapor, it is densest at the meniscus, and is gradually lost to the eye upward. If it is in the liquid, the same is true in the opposite direction. How far the eye can follow it depends on the amplitude of the vibrations.

In the theoretical case of perfect equilibrium between the two phases we can think of no cause for such a phenomenon except gravity, whose influence would be equivalent to that of slightly greater pressure in the lower part of each phase than in the upper, and would result in so far in a maximum tendency to condensation at the bottom of the vapor, and in a maximum tendency to the formation of vapor at the top of the liquid. In any attainable approximation to perfect equilibrium, the meniscus, where the two phases are in contact with each other, is of course the region of greatest saturation, and ought therefore to be most sensitive.

In any case, one useful effect of this thickening of dynamic fog toward the meniscus is to define the position of the latter with great precision. Particularly is this true when the fog lies on both sides of it. Such an aid to observation gains increasingly in value as the critical temperature is approached and the meniscus itself becomes thinner, flatter and all but invisible. In fact — and this was a great surprise — even in our most careful experiments it was possible to define the boundary between phases (?) at a temperature .15 of a degree above the point at which the meniscus became entirely invisible. No attempt was made to determine for how long a time this fog line would continue above the critical temperature. But it was noted several times after a lapse of 15 to 20 minutes, and once after about half an hour. Within these time limits at any rate it never failed to appear as a result of proper bowing. Its density however was very slight. In fact the point of maximum density in dynamic fog appears to lie about one tenth of a degree below the critical temperature, as has been said, and the sensitiveness decreases very rapidly from this point upward.

Critical Temperature of Carbon Dioxide.

As the carbon dioxide which was employed in these experiments was of rather unusual purity, containing only from two ten-thousandths to twenty-five millionths of gas unabsorbed by potassium hydroxide,[1] it may be of interest to record observations which were made of its critical temperature.

Of course the ideal position for the thermometer in such determi-

[1] The preparation of this gas will be described in a subsequent paper.

nations is inside of the pressure tube itself, wholly immersed in the substance under examination. But this was impossible under the circumstances, and the method employed was the usual one of raising and lowering the temperature of the bath very slowly indeed, and noting the point at which the meniscus disappeared and reappeared. The lag of the carbon dioxide was corrected in part by occasional firm bowing. The average differences of temperature between the disappearance and the reappearance of the meniscus was .08 of a degree, and the mean value of the critical temperature itself was 31.26° (cor.). The thermometer was standardized by the use of fused sodium sulphate crystals, the transition point of which was taken as 32.383°.[1]

WESLEYAN UNIVERSITY,
MIDDLETOWN, CONN.,
February 6, 1908.

[1] Zeitschrift für physikalische Chemie, *43*, 1903, 471.

RADIOACTIVITY OF A SMOKE LADEN ATMOSPHERE.

By S. J. Allen.

IN this paper are expressed a number of results obtained on the radioactivity of the air at Cincinnati during the past year. Since the radioactivity of the atmosphere is such a wide-spread phenomenon, and differs both in amount and rate of decay in different localities, it is of interest that as many observations as possible be made under varying climatic conditions.

Some years ago at Montreal, the author made a series of observations [1] on the rate of decay and found it to be approximately exponential, falling to half value in about 45 minutes. On several occasions, however, the period varied from 38 to 60 minutes and some indications were obtained of an even slower rate of decay. It was then suggested that the general rate of decay was not simple but the resultant of several rates of decay each differing from the others.

Since that time observations have been made by various investigators in different parts of the world, all leading to the same result that the rate of decay in general is not simple. Bumstead and Wheeler [2] at New Haven showed that the air drawn from the soil a that place contained radium emanation, and by exposing a negatively charged wire, obtained on it an excited activity identical with that due to radium. It was also shown that a small amount of thorium-excited activity was present. Blanc [3] working at Rome found that the activity on a negatively charged wire after a long exposure, showed clearly the presence of thorium-excited activity.

Eve [4] at Montreal has made a number of investigations on the radioactivity of the atmosphere and has obtained evidence to show that the amount of radium emanation present in the free atmosphere

[1] S. J. Allen, Phil. Mag., 1904.
[2] Bumstead & Wheeler, Am. Jour. of Science, 1904.
[3] Blanc, Phil. Mag., 1906.
[4] Eve, Phil. Mag., 1907.

is of the right order of magnitude to account for the greater part of the effects observed. Quite recently he has shown by a direct experiment the presence of the emanation in the free air.

The air at Montreal in the winter time is generally very dry, cold, and free from smoke particles, whereas the conditions at Cincinnati are quite the reverse, the amount of finely divided smoke particles in the air being very large. The object of the present investigations was to obtain a large number of decay curves under different atmospheric conditions, and by comparing one with the other, and analyzing them, to obtain if possible the simple rates of decay common to one or more.

If the radioactivity of the atmosphere is due to the presence of radium, thorium, and possibly actinium distributed throughout the crust of the earth, we would naturally expect the rate of decay to be in general very irregular and to be made up of the separate rates of decay of the excited activities of the above radioactive elements. Since the rate of decay of the radium emanation is slow, falling to half value in about 3.86 days, there would be time for it to diffuse uniformly throughout the atmosphere and to a considerable height above the earth, and yet retain a sufficient amount of activity to cause the results observed. On the other hand the emanations of thorium and actinium decay too rapidly for them ever to reach very far, if at all, above the earth. That part of the radioactivity of the air which is due to radium and thorium must be occasioned by their excited activities, and not their emanations.

We would thus expect the activities due to radium to be always present and to constitute the larger amount, while the effects due to the thorium and possibly actinium would be very irregular both in occurrence and amount.

It is then possible to have present in the free atmosphere radium emanation, radium A, radium B and radium C; thorium A and thorium B, and possibly actinium A. The radioactivity as obtained on a suspended wire might consist of one, or a combination of several of these activities and be of course in general irregular.

In the present investigation an endless copper wire running over two insulated wooden pulleys was used to collect the radioactivity from the air. The inner pulley was fastened inside the laboratory,

the two wires passing through two holes in a sheet of ebonite placed under a window. The other pulley was fastened to a building about 180 feet away, the insulation of this pulley being protected from the rain, snow and moisture by a metal hood. By rotating the inner wheel the activity could be removed quickly from the wire without going outside the building. The distance of the wire above the ground was about twenty feet.

The wire was used under three conditions:

1. It was charged negatively by an influence machine up to potentials of 5,000 to 40,000 volts.

2. It was charged positively.

3. It was not charged at all.

The radioactive substance obtained on the wire was removed in several different ways.

(*a*) A piece of leather moistened with ammonia was rubbed over the wire.

(*b*) A piece of wood with a groove cut to fit over the wire, and moistened with ammonia, was used.

(*c*) A piece of lead wire, suspended underneath the copper wire during exposure, was afterwards wound on a form into a flat spiral and tested.

(*d*) A piece of fine linen was rubbed lightly over the wire without any ammonia.

The rate of activity decay was obtained in the usual manner by placing radioactive substance between two condenser plates and observing the saturation current as time went on. The first observation was taken from two to five minutes after removal of the charge from the wire. The ionization current was measured by a Dolezalek electrometer. In the early experiments the "rate of leak" method was used, but in the later ones the null method as incorporated by the author in his new null reading instrument.

This instrument is fully described in a recent article[1] and it will not be necessary to go into details here. A consideration of Fig. 1, will, I think, show clearly the working of the instrument. The quantity of electricity furnished to the charging quadrants by the radioactive substance is neutralized by an equal amount of opposite

[1] S. J. Allen, Phil. Mag., Dec., 1907.

sign obtained from an adjustable standard of uranium oxide. The standard is calibrated in proportional numbers, the maximum being taken as 100 per cent.

The balance point is independent of the capacity of the system and of the sensitiveness of the electrometer. The electrometer is thus only used as an indicating and not as a measuring instrument. With this apparatus the intensity of activity is obtained at the exact

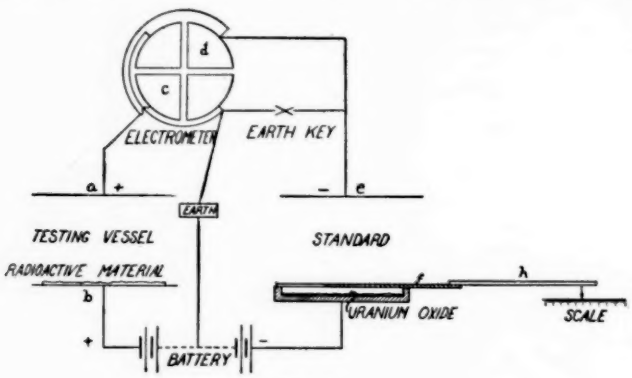


Fig. 1.

instant of time considered, while in the "rate of leak" method, some little time is necessary to make a reading. Moreover the readings from day to day are always obtained in terms of a definite standard and are thus directly comparable with one another.

The error of observation in these curves is probably not greater than one per cent.

About fifty curves in all were obtained under varying conditions of the atmosphere, from a clear, dry, cold day, to a warm, moist and smoky one. On all occasions and under all conditions of collecting a measurable amount of raidioactivity was obtained. When the wire was charged negatively, the largest amount was observed, as one would expect. When the wire was charged positively only a small amount was obtained, while for an uncharged wire a very considerable quantity could be always collected. The maximum amount on the uncharged wire was as much as 30 per cent. of the maximum of that on the negatively charged one. Over a gram of soot could sometimes be collected on the wire, which was as active weight for weight as uranium oxide.

It was found that a piece of linen rubbed very lightly over the wire removed practically all the active substance in the case of the uncharged wire, but only 50 to 80 per cent. for the negatively charged wire. To get the remainder off the wire had to be rubbed over with a piece of cloth or leather moistened with ammonia. In the case of the charged wire the strong field draws some of the active carriers into close connection with the metal, while with the uncharged one the active substance is deposited lightly on the surface.

The interesting fact that the activity can be obtained on an uncharged wire is undoubtedly due to the presence of the finely divided

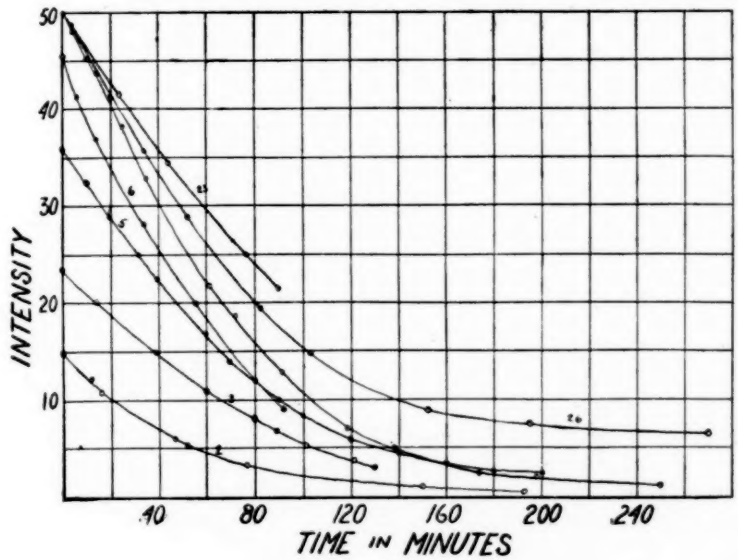


Fig. 2.

smoke particles in the air, as no such phenomenon was observed at Montreal, where the air is comparatively free from smoke. These particles act as collectors for the radioactive carriers. In falling through the air they carry with them the active matter, and are deposited on any surface they come in contact with. The results are similar to those observed by Miss Brooks[1] for the excite dactivity of radium in the presence of dust particles. The activity of snow and rain is also due to the same cause. The snow and rain coming

[1] Miss Brooks, Phil. Mag., 1904.

from a high altitude would probably only contain radium C, while the activity of the smoke particles being from a much lower altitude would be much more complex.

The period of decay of the activity from rain and snow as shown by the author and others is about thirty minutes, very close to that

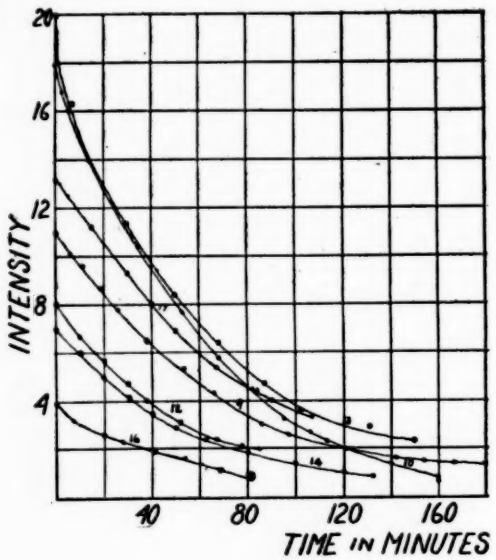


Fig. 3.

of radium C, whereas as I shall presently show the period of decay for the activity near the earth varies from 36 to 80 minutes.

The results of the complete set of observations are expressed in the decay curves shown in Figs. 2–7. The ordinates represent the saturation currents in arbitrary units, and the abscissæ the times in minutes. Those curves which have the intensity plotted in per cent. are the ones made with the null instrument, while the others represent those by the "rate of leak" method.

In Table I. the data taken from these curves are expressed in a more convenient form for comparison. The intensities are all expressed in per cent. of the reading when the time is equal to zero. The numbers in the first column refer to the number of the curves in Figs. 1–8. Under "Remarks" are given some data as to the method of collecting and removing the active substance from the

TABLE I.

Intensity in Per Cent.

No.	80	60	50	40	30	25	20	12.5	6.3	3.1	Remarks.
1	21	42	54	68	83	93	103	125	164	230	Thin leather with ammonia
*2	12	24	36	48	60	70	80	112	166		Thick leather with ammonia
3	20	43	55	70	86	97	108	132			Thick leather with ammonia
4	18	38	49	62	79	89	102	122	160		Thick leather with ammonia
5	20	42	56	69	85	96	111	139	195		Thick leather with ammonia
6	15	35	46	61	75	83					Thick leather with ammonia
7	16	39	54	64							Thin leather with ammonia
8	13	30	42	56	67	80	94	122	163		Thick leather with ammonia
9	17	38	50	64	82	91	110	167			Lead wire — signs of slow rate of decay
10	17	35	44	56	70	78	90	118	150		Lead wire
11	17	37	48	60	77	82	94	122			Lead wire
*12	13	28	37	50	69	82					Lead wire
13	18	33	45	60	79	90	108	148		1200	Lead wire — signs of slow rate of decay
*14	14	29	39	52	68	79	100	124			Lead wire — signs of slow rate of decay
15	19	39	49	65	86	100	116				Lead wire — signs of slow rate of decay
*16	10	28	39	50	63	73					Wood with ammonia
17	19	40	52	66	90	109					Wood with ammonia, signs of slow decay
18	20	39	50	65	81	100					Wood with ammonia
*19	10	28	40	55	76	85	99				Wood with ammonia
20	22	44	57	70	86	94	104	131			Linen, wire charged negative, without ammonia
21	20	41	51	62	76	86	98	118			Linen, wire charged negative, without ammonia
22	25	55	72	88	107	119	132	163	220		Linen, wire charged 2 hours negative, without ammonia, slow decay
23	28	59	77	98							Linen, wire charged negative, without ammonia, after 16 hours 10 per cent. left
24	16	37	48	60	78	86	95	116	150	194	Linen, wire charged 30 minutes negative, without ammonia
*25	11	29	40	52	72	86	98				Linen, wire charged 5 hours negative, without ammonia
26	22	47	62	79	101	117	137	350			Linen, wire charged 21 hours negative, without ammonia, after 20 hours 4 per cent. left
27	16	30	42	60	80	94	110	120			Linen, wire uncharged, slow rate of decay
*28	15	31	39	53	71	83	99	132			Linen, wire uncharged
29	12	31	44	58	80	92				1140	Linen, wire uncharged, slow rate of decay
30	18	38	48	56	78	87	104	140			Linen, wire uncharged, slow rate of decay
31	18	41	79	134	410						Linen, wire uncharged, after 24 hours 10 per cent. left
32	14	34	45	62	81	94	112	165			Linen, wire uncharged, after 6 hours 8 per cent. left
*33	8	26	38	56	76	89	108	138	172		Linen, wire uncharged, raining
34	21	46	64	87	112	129	150	200		1200	Linen, wire uncharged, slow rate of decay
35	12	38	43	59	79	89	106	133			Linen, wire uncharged, rain and snow
39	10	30	43	59	79	90	102	120	175	380	Linen, wire uncharged, slow rate of decay
40	13	36	52	70	90	103	118	150			Linen, wire uncharged, slow rate of decay
*41	12	28	40	54	72	82					Linen, wire uncharged
*42	12	27	39	51	68	79	93	117			Linen, wire uncharged
*43	12	26	37	47	62	74	88	112			Linen, wire uncharged
*44	12	27	37	47	62	73					Linen, wire uncharged

TABLE I.—*Continued.*

Intensity in Per Cent.

No.	80	60	50	40	30	25	20	12.5	6.3	3.1	Remarks.
45	18	37	48	60	75	84	97	120	156		Linen, wire uncharged
46	22	37	45	54	69	78	92	114			Linen, wire uncharged
47	18	39	52	64	81	90	104	130			Linen, wire uncharged
48	22	41	51	62	75	82	91	112	146		Linen, wire uncharged
49	8	22	35	49	67	78	93	132			Linen, wire uncharged, slow rate of leak
50	20	35	43	54	66	76	86	108			Linen, wire charged 1 hour
51	14	30	40	52	67	76	90	120			Linen, wire charged 2.5 hrs., after 19 hrs. 2.3 per cent. left
*42a	12	27	38	52	68	80	95	116			This curve is the mean of curves marked *

wire, time of exposure and duration of activity. The figures in the intensity columns represent the times taken for the activity to decay to various percentages of the maximum. The time taken to fall to 50 per cent. we will call the period of decay.

A glance at the curves shows at once the extreme irregularity both in shape and period of decay. From Table I. under 50 per cent. we see periods ranging all the way from 36 minutes to 79

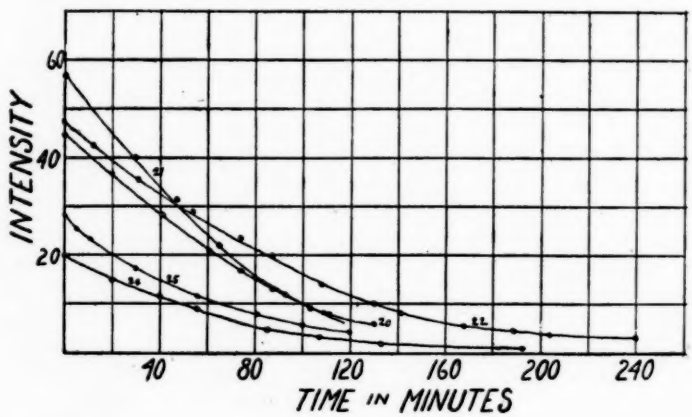


Fig. 4.

minutes. Only one curve 42, Fig. 7, is truly exponential over any great length of time, this having a period of about 38 to 39 minutes.

A study of these curves brings out the fact that they can mostly be grouped under three heads :

1. Exponential, or approximately so, and capable of being represented by an equation of the familiar form,

$$I_t = I_0 e^{-\lambda t}.$$

2. Curves like 48 and 50, consisting of a convex upward part at first, and then of an approximately exponential part having a period of about 30 minutes.

3. Those having at first a more rapid decay, and afterwards a slower one extending over several hours, the period of this last being about eleven hours.

In examining the periods as expressed in Table I., it is seen that eleven curves (2, 12, 14, 16, 19, 25, 28, 33, 41, 42, 43, 44) can be

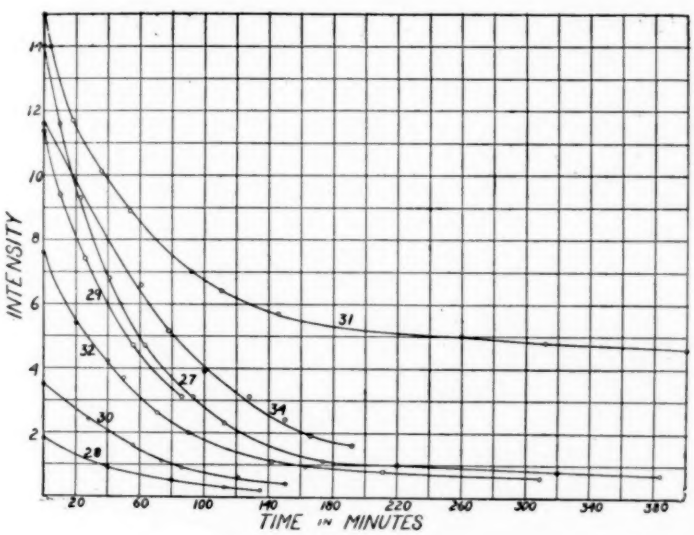


Fig. 5.

classed under head (1) as being approximately exponential and having a period of 36–40 minutes. None of these curves shows any appreciable amount of the slow rate of decay. Curve 42*a* represents the mean of these curves and it is nearly identical with 42 (the exponential one), having a period of 38 minutes.

The agreement between these curves is certainly not accidental and represents a simple and common rate of decay. One cannot identify it with any of the simple rates of decay of the active deposits

from the radioactive substances. It may be, and probably is, a mixture of radium B and radium C in invariable proportions. It is, however, worthy of note that actinium A has a period of about 36 minutes.

The curves under head (2) are very similar in general shape to the curve of decay of the excited activity due to radium (leaving out the first rapid stage), and are probably caused in part by the

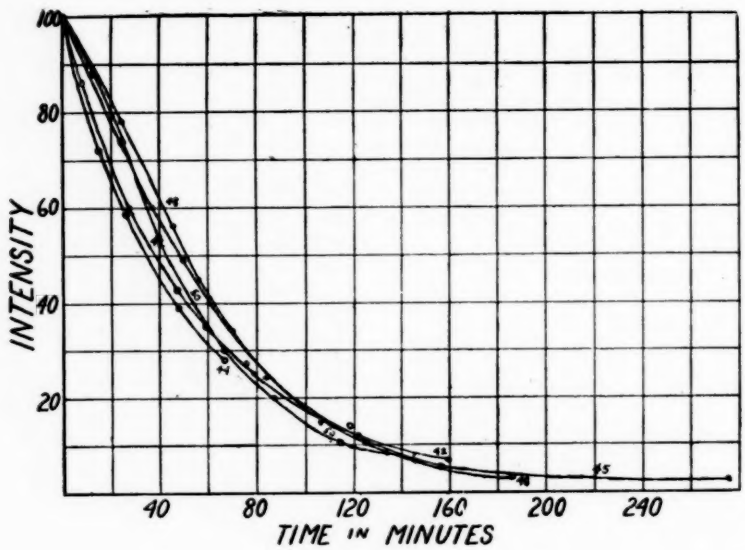


Fig. 6.

radium emanation present in the air. The exponential part of these, having a period of decay of about 30 minutes, shows very good agreement with radium C. These curves were obtained for both the charged and uncharged wire and in the two cases represent the maximum amount of activity collected during the entire series.

The curves classified under head (3) do not differ materially from those already discussed, except that they have superimposed on them a very slow rate of leak of about eleven hours period. This slow rate of leak is identical with that of thorium A and is unquestionably due to it. It is not always present, and can be obtained on an uncharged as well as a charged wire.

On some days the uncharged wire was first rubbed over with a piece of linen, then charged negatively for a certain time and the two active deposits tested. Under these conditions whenever the slow rate of decay was present in one, it also appeared in the other. It

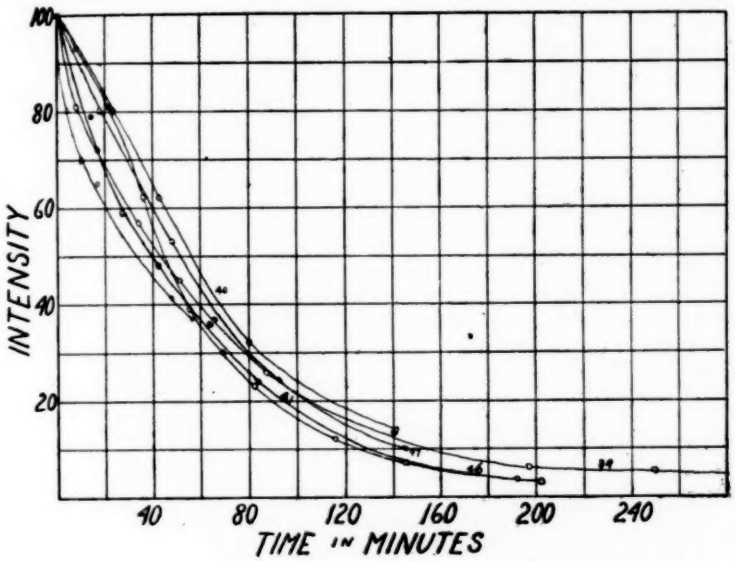


Fig. 7.

could be obtained for a short exposure of the wire as well as for a long one, though naturally in the latter case under the same conditions the amount was greater than in the former.

TABLE II.

No.	100	50	25	12.5	6.3	
13 & 29	0	37	72	101	129	c''
26	0	44	90	122		f''
32	0	39	75	105	136	c'''
34	0	54	104	141	176	f
31	0	28	54	86	111	c
51	0	37	67	97	128	f''
39	0	41	82	111	136	f'''
23	0	54	92			c'

If this slow rate of decay is due to thorium A and the amount of it be known at any time after the start, the amount at any other

time can be easily calculated from the equation $I_t = I_0 e^{-\lambda t}$, representing the decay of thorium A. This rate of decay can then be subtracted from the actual observed rate, and the net decay obtained. I have done this for nine curves, which show to a marked degree the amount of thorium A present, and the results are shown in Figs. 8 and 9. For example, curve (*a*), Fig. 8, represents the actual curve observed; curve (*b*) that of the thorium A present, while curve (*c*) shows the net decay. It is interesting to note that

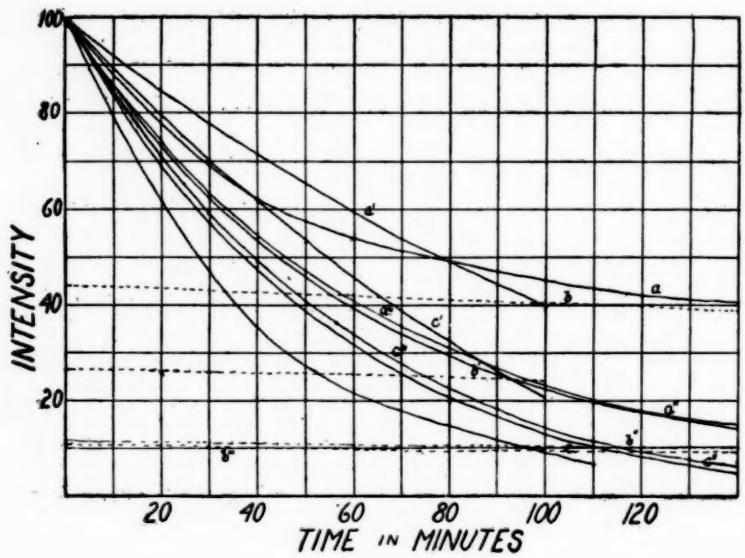


Fig. 8.

this curve (*c*) is very approximately exponential and has a period of from 26 to 28 minutes. It is somewhat difficult to estimate with accuracy the amount of thorium A present, which will probably account for the departure of the curve from the exponential towards the bottom, where the amount of thorium A is more than comparable with the remainder. The upper part of the curve is therefore the most accurate. The actual curve consequently consists of a mixture of the simple decays of thorium A and radium C. In this case the amount of thorium A present is about 44 per cent. of the total.

The rest of the curves in Figs. 8 and 9 have been treated in the same manner. The amount of thorium A present in the various

curves varies greatly in proportionate amount. For the sake of comparison, the results are collected in Table II., which is of the

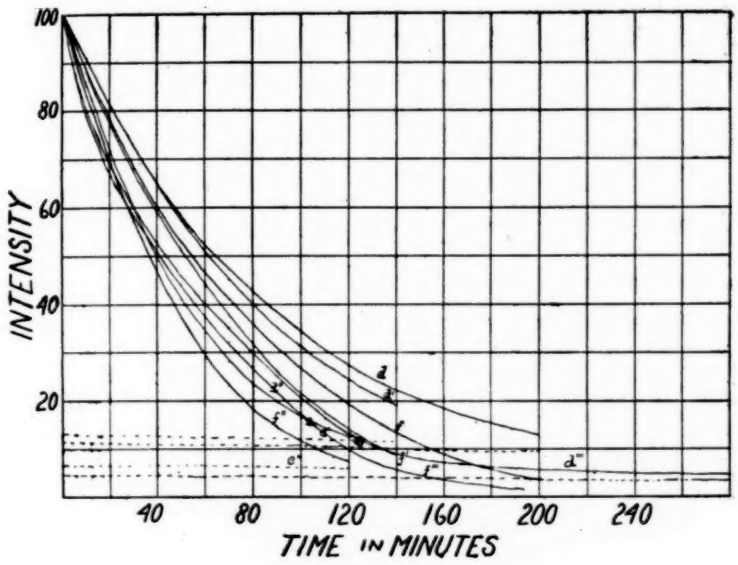


Fig. 9.

same character as Table I. The periods are given under column headed 50. It will be noticed on examination of this table, that, although the periods for the first part of the curve differ considerably, towards the end they all approach about 30 minutes. With the exception of curve (c) they are all complex, but show the presence of radium C. Two of them (f) and (c') show the presence of a slower rate of decay.

TABLE III.

No. of Curve.	Periods.	No. of Curve.	Periods.
42	39, 40	34	54, 39
40	52, 36	51	38, 30
45	56, 41, 36	39	28, 54
31	28	4	51, 40, 31
13 and 29	33, 29	8	42, 38
32	34, 29		

These curves, and several others free from thorium A, were plotted with the logarithms of the intensities as ordinates, and the

periods calculated. The results are shown in Table III., which gives the component periods as far as could be obtained. With one or two exceptions these can be put in three classes, viz:

1. Period 28–31 minutes, due to radium C.

2. Period 37–40 minutes, due to the same cause as those 11 curves already discussed, probably a mixture of radium B and C, possibly in some cases actinium A.

3. Period 52–56 minutes, cause not apparent. (Thorium B has a period of about this amount.)

In conclusion, I think it can be safely stated, that the curves of decay for the excited activity of the atmosphere, where large quantities of smoke particles are present, will show many irregularities, but may be analyzed into component parts, which agree with the rates of decay of the excited activities of the radioactive substances, radium, thorium and possibly actinium.

Also the radioactivity under these conditions can to a large extent be collected on an uncharged wire, being carried there by the settling of the smoke particles. The activity due to the radium is always present, while that caused by the thorium is much more variable, and often absent, or at least in inappreciable quantities.

UNIVERSITY OF CINCINNATI,
January, 1908.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

THEORIES OF THE COLOR OF THE SKY.[1]

BY EDWARD L. NICHOLS.

IN asking your attention to-day, even briefly, to the consideration of the present state of our knowledge concerning the causes of the color of the sky it may be truly said that I am inviting you to leave the thronged thoroughfares of our science for some quiet side street where there is little going on and you may even suspect that I am coaxing you into some blind alley, the inhabitants of which belong to the dead past. Nevertheless, the problem is not a simple one. It cannot be considered as settled or likely to be soon completely solved.

REVIEW OF EXISTING THEORIES.

It is true that the theory suggested by Brücke,[2] appears to many minds conclusive and all sufficient. The famous demonstrations of Tyndall[3] and the masterly theoretical work of Rayleigh[4] may be said to have established Brücke's view that the color of the sky is that of a turbid medium. More recent experimental work has been in a general way confirmatory of this theory.

At the same time it should not be forgotten that other explanations of the color of the sky have been offered. Clausius[5] in a classical paper, has shown that the color of the sky is deducible on theoretical grounds from the assumption of the existence of minute vesicles or water bubbles suspended in the air. Hagenbach[6] has pointed to the reflection from surfaces of moving bodies of air as the probable cause of the blueness of the sky. Spring[7] has called attention to the fact that oxygen, ozone, water and hydro-

[1] Presidential address delivered at the New York meeting of the Physical Society, February 29, 1908.

[2] Brücke, Poggendorff's Annalen, LXXXVIII., p. 363, 1852.

[3] Tyndall, Proc. Royal Society, XVII., p. 223, 1868; also Phil. Mag. (4), XXXVII., p. 388.

[4] Rayleigh, Phil. Mag. (4), XLI., pp. 107 and 447, 1871.

[5] Clausius, Pogg. Annalen, LXXVI., p. 161; LXXXIV., p. 449, 1849.

[6] Hagenbach, Pogg. Annalen, CXLVII., p. 77, 1872.

[7] Spring, Bulletins de l'Academie Belge (3), XXXVI., p. 504.

gen peroxide, all of which are constituents of our atmosphere are blue, and that they are present in sufficient quantity to amply account for the preponderance of the shorter wave-lengths in the light which reaches us from the atmosphere. Lallemand[1] and also Hartley[2] have sought for an explanation in the fluorescence of the ozone of the upper atmosphere, and finally subjective color[3] has been advanced as a possible explanation.

Of these various theories only that of Clausius can be discarded without further consideration. That the atmosphere is a turbid medium we have overwhelming experimental evidence but that this turbidity is in itself the sole source of color does not necessarily follow. It has been a characteristic of nearly all the literature of this subject that each author has emphasized some one explanation to the exclusion of all others, although Pernter[4] who is one of the most strenuous advocates of the theory of turbidity, is inclined to consider the fluorescence of ozone as a possible additional factor. Jansen[5] alone, so far as I know, in an interesting summary of the literature of the subject treats the color of the sky as due to the combination of a number of factors.

We may state the case as follows:

1. The turbidity of the atmosphere would of itself give us a blue sky, but the ideal medium of Rayleigh would afford a distribution of intensities to which the actual sky rarely if ever corresponds.

2. Even were the atmosphere free from particles of dust, condensed water vapor or other extraneous matter it would not, according to Rayleigh's latest paper, be optically empty, to use the term employed by Tyndall, but would be blue by virtue of reflections from the molecules of the air itself.

3. If there were no other source of blueness, the color of the air, according to Spring, would give us a blue sky by virtue of the selective absorption-color of various of its constituents. The objections to the adoption of this as a factor are obvious and are regarded by many writers as insuperable but their arguments are not in my opinion conclusive.

4. Reflection from surfaces in a troubled atmosphere as pointed out by Hagenbach, would give us light from the sky increasing in intensity relatively to sunlight in proportion to the square of the wave-length. This is quite sufficient to account for the average blueness of the sky but not for the intenser blueness frequently observed. It cannot therefore be regarded as the sole or most important factor.

[1] Lallemand, Comptes Rendus, LXXV., p. 707, 1872.

[2] Hartley, Nature, XXXIX., p. 474, 1889.

[3] Nichols, Phil. Mag. (5), VIII., p. 425, 1879; also Trans. Kansas Acad. of Science X., p. 111.

[4] Pernter, Denkschriften d. Akad. d. Wissenschaften zu Wien, LXXIII., p. 301, 1901.

[5] Jansen, Das Weltall, V., 1904–5, p. 37 et seq.

5. Fluorescence as a factor of blueness of the sky cannot be definitely considered at the present time for lack of experimental data concerning it.

6. As regards the subjective or physiological factor it may be said that were there no other cause the sky would undoubtedly appear blue; for we still see it blue where measurements with the spectrophotometer indicate a composition relatively much weaker in the shorter wave-lengths of the spectrum than the *average* composition of sunlight. In the present paper I shall, however, consider only the objective factors.

The problem of the color of the sky resolves itself then into a determination of the relative importance of these various factors, the existence of all of which with the possible exception of fluorescence must be regarded as experimentally established. Such an analysis is unfortunately a difficult matter on account of the complexity of the phenomena and because the observer cannot create his conditions nor hold them constant.

The phenomena of aerial polarization indicate beyond any doubt the turbidity of the air as one source of the blueness of the sky. In the case of the ideal turbid medium of Rayleigh, in which all the particles are small as compared with the wave-length of light, the composition of the diffused light, as is well known, is such that the ratio of the intensity of the reflected ray to that of the incident ray varies inversely as the fourth power of the wave-length. This would give us a sky about twelve times as bright in the extreme violet as in the red, as compared with sunlight. Rayleigh's analysis may be said to have found complete verification in the experimental study of artificial turbid media, particularly in the studies of the colors of the steam jet by Bock.[1] Spectrophotometric measurements of the sky itself have, however, led to widely varying results. Zettwuch,[2] who made many measurements of the sky at Rome, calls especial attention to its extreme variability. Crova,[3] who has made more measurements of this sort than any other investigator with whose work I am acquainted, obtained, in the course of measurements at Montpellier extending over more than two years, relations for the variation of intensity with wave-length in which the exponential constant ranged from 1.61 to 6.44. Crova's measurements unfortunately extend only through the brighter parts of the spectrum from .635 μ to .510 μ; the extreme red and the violet being omitted. If, however, we are to accept his exponential coefficients as even approximately correct, we shall have to admit other sources for the blue of the sky than that of turbidity. That there is further evidence to the same effect will be shown later.

[1] Bock, Wiedemann's Annalen, LXVIII., p. 674, 1899.

[2] Zettwuch, Philos. Magazine (6), IV., p. 199, 1902.

[3] Crova, C. R., CIX., p. 493; CXII., p. 1178; also Annalen de Chimie et de Physique (6), XX., p. 480.

SOME DETERMINATIONS WITH THE SPECTROPHOTOMETER.

Certain measurements with a portable spectrophotometer, which I have undertaken in various localities, during a recent vacation may be of interest as indicating the nature of the phenomena with which we have to deal even if they afford insufficient data for the solution of the general question.

Comparisons of the light from the sky with direct sunlight by means of the spectrophotometer are chiefly interesting as a means of determining the relation between actual skies and the ideal sky imagined by Rayleigh. For other purposes such measurements are of little value on account of the variable quality of sunlight after passage through the earth's atmosphere, and because the sky receives a portion of its illumination from light reflected from clouds and from the surface of the earth; and further because of absorption which the blue light from the sky suffers from the turbid medium itself. To indicate the variations in the quality of sunlight which are encountered in making direct comparisons of sky and sun I may say that the range in the relative intensity of sunlight when compared with the acetylene flame employed as a standard source in my measurements was between 9.9 at Brienz, Switzerland, on August 19, 1907, and 10.2 at Andermatt on August 9 of that year, on the one hand, and 3.57 at Brienz on August 13, where these quantities express the intensity of the sun's spectrum in the violet (.418 μ) as compared with the spectrum of the standard flame. Both spectra were taken of equal intensity in the red at .725 μ.

Measurements of artificial turbid media are not open to this difficulty. Bock, whose steam jet, made turbid by the action of hydrochloric acid gas, seems to have afforded the most favorable conditions for investigation, found the following relative intensities, the intensity in the red being taken as unity:

Red	1.00
Yellow	1.52
Green	2.89
Blue	4.35
Violet	9.81

Rayleigh's formula for the ideal medium gives for the corresponding regions:

Red	1.00
Yellow	1.98
Green	2.82
Blue	4.92
Violet	8.50

Bock also made comparisons between sky and sun and found on five successive days the relative intensities of the violet, as compared with

red, to be as 5.7, 8.7, 6.5, 5.2, 4.3. Of these only one shows an approach to the ideal value.

In comparing the spectrum of the skylight with that of an artificial standard, the flame sources hitherto employed, namely, the petroleum flame, by Vogel; the Carcel flame, by Crova; and the Hefner flame, by Frl. Köttgen; are too weak in the violet to admit of satisfactory measurements in that region. The acetylene flame which I have employed in my recent experiments is better in this respect, being relatively about three times as bright in the violet as the sources previously employed, and I have attempted to cover a much wider range than earlier observers, namely, from .725 μ in the red to .390 μ in the extreme violet. It is in these regions at the extreme ends of the visible spectrum, hitherto uncovered by spectrophotometric observations, that some of the most interesting and striking variations of the light from the sky occur.

The instrument employed was planned with special reference to portability. It consists essentially of a simplified Lummer-Brodhun spectrophotometer with a vertical collimator *V*, containing a nicol *N*, and a horizontal collimator *H*, as shown in Fig. 1. For the single prism of the

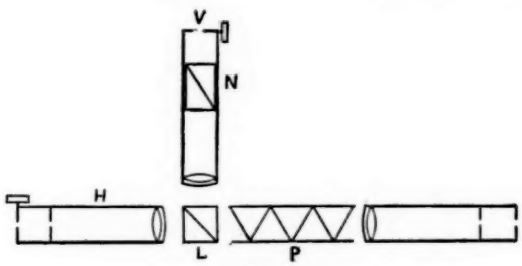


Fig. 1.

original instrument a set of direct vision prisms *P* is substituted. The comparison source is a small flat acetylene flame surrounded with a hooded chimney of black metal. In front of the flame is a diaphragm with an aperture of 2 mm. diameter so that only the central portions of the flame send light to the slit. About 3 cm. in front of this diaphragm is a circular screen of milk glass which within the limits of the visible spectrum exhibits no marked selective absorption. This lamp is mounted in front of the horizontal slit of the spectrophotometer and access of all light from other sources is excluded by screens.

The acetylene lamp is supplied from a small portable generator and a light rubber bag is used as a storage reservoir and to equalize the pressure of the gas supplied to the flame. Such a comparison source does not realize the conditions as to uniformity of intensity which can be obtained in the laboratory but the variations were rarely troublesome and indeed the

degree of constancy was quite sufficient for the purposes of studying so variable a spectrum as that which we obtain from the sky.

Numerous measurements of the spectrum of the sky in various localities by means of this apparatus showed, in general, far greater relative intensities of the longer wave-lengths than one would expect from the theory of Rayleigh. Direct comparisons of skylight and sunlight made by substituting for the standard flame a screen smoked with magnesium oxide and exposed to the sun's direct rays, with adequate precautions to prevent

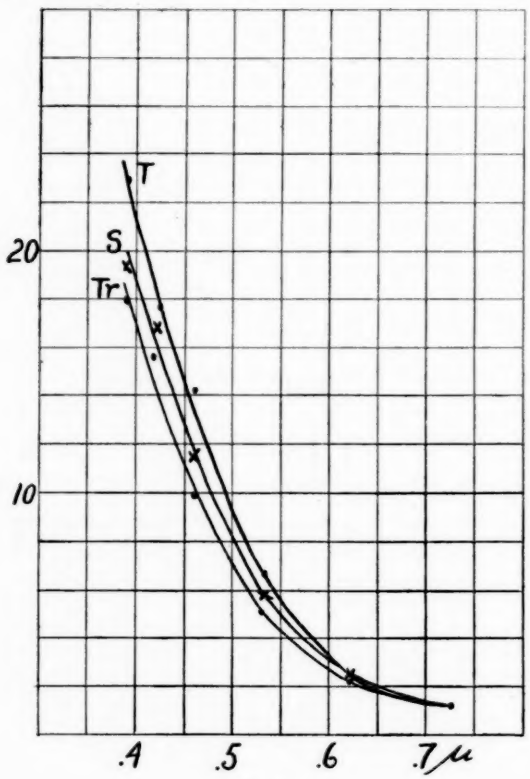


Fig. 2.

illumination from other sources, showed that the skies under consideration were as a rule very far from corresponding to the light which would be obtained from an ideal turbid medium.

Among the most obvious causes of such discrepancies are:

(*a*) The presence of larger reflecting particles in the atmosphere, sometimes invisible and sometimes forming masses of mist or cloud.

(*b*) Absorption by transmission through the turbid medium itself.

(*c*) Illumination of the atmosphere by light reflected from the surface of the earth.

To determine definitely and quantitatively the relative importance of these and other possible factors is a matter of great difficulty; but the study of numerous curves obtained under different conditions throws some light upon the question. It was found that curves taken at dawn and in the twilight after sunset showed a much greater relative preponderance of blue than those taken during the day. These curves moreover were all of the same type and in close agreement with each other as regards the distribution of intensities. In Fig. 2 a group of such curves is given, all reduced for comparison to equal intensity in the extreme red.

While it is impossible to make a direct comparison between such spectra observed at dawn or twilight with the spectrum of the rays by means of which the sky overhead is illuminated, an indirect approximate estimate may be made by means of comparisons made during the day immediately following or immediately preceding, as the case may be, of sky and lamp and then of sky and sun. From several such computations it appears that the skylight curves at dawn and twilight not only show far greater constancy of type than do mid-day measurements, but also a fair approximation to the *ideal* sky. I found for example from measurements made at Sterzing (Tyrol) on July 18 at 4:55 A. M. (before sunrise) and the comparison of these with measurements on the same day between 8 and 9 A. M., in which ratios between sky and lamp on the one hand and sky and sun on the other were obtained, that the probable early morning sky/sun ratio was 8.9 at wave-length .418 μ both being reduced to unity at .725 μ. The ratio for the ideal sky after Rayleigh's formula for these wave-lengths is 9.3.

Since these dawn-twilight skies by fair weather show but litttle variation as to composition I have taken the average of the data at my disposal and have called the resulting curve the *typical dawn curve.* For convenience this is arbitrarily given an intensity of unity in the extreme red (.725 μ) and other ordinates express the ratio of the skylight to the light from the flame, wave-length for wave-length, throughout the spectrum. The characteristic difference between the typical dawn curve, or any individual dawn curve by fine weather, since these are found to agree closely in composition, and the spectrum of the sky in the middle of the day referred to the same comparison source is shown in Fig. 3. It will be seen that while the skylight taken as a whole is greatly increased in intensity the actual intensity of the blue and the violet is much less affected than are the longer wave-lengths.

The gradual change in the quantity and character of the light from the sky as the sun rises in the heavens is shown in Fig. 4, which contains curves obtained at Sterzing (Tyrol) at 4:45 A. M., before sunrise (*a*), at 5:40, soon after sunrise (*b*), at 7:00 (*c*) and at 8:25 A. M. respectively, on a cloudless and unusually clear morning.

This relation of curves taken after sunrise, to the typical dawn curve is more obvious if we plot the ratios of the curves to be compared for each wave-length of the spectrum. The results for curves *b*, *c* and *d* of Fig. 4 are given in Fig. 5.

These curves of ratios are significant because they repeat themselves persistently as to type, although with certain systematic variations, in the case of numerous measurements taken in various localities.

In fine weather, especially in summer, the moisture of the atmosphere tends to condense and to form masses of sunlit cloud which gather in the

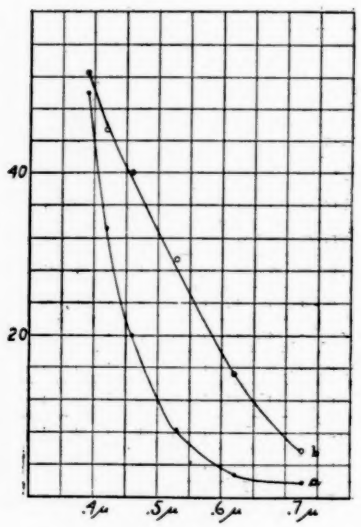


Fig. 3.

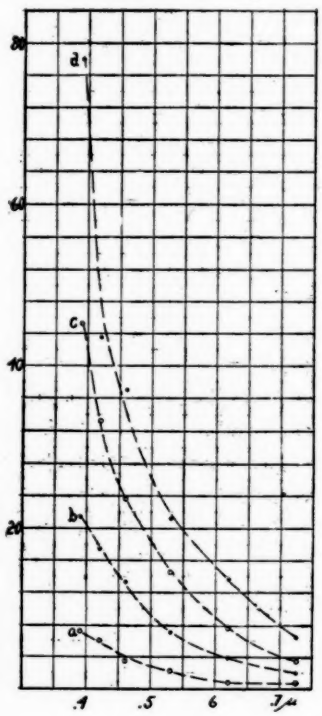


Fig. 4.

middle of the day and disappear towards sunset. The sky/acetylene curve then takes on another distinctive form well illustrated in Fig. 6. The two curves there shown were taken at Sterzing about two hours after the completion of the set of morning measurements plotted in Fig. 4.

Fig. 7 shows the culmination of this effect in the curve for 1:30 P. M. obtained from a very bright sky with masses of cumuli, its persistence with much reduced intensities at 5:50 P. M. and its almost entire disappearance at 6:45 P. M. The two curves for 7:20 and 7:40 P. M. —

about sunset — show complete return to the early morning type. This form of curve is especially characteristic of summer weather in the mountains and the droop towards the ultra-violet was most pronounced in high localities, as at Andermatt, Samaden (Engadine), on the Rhone Glacier and on the Brienzer Rothhorn. It occurred occasionally, but in less fully developed form in the winter skies of Algeria and Sicily.

The study of the sky, on foggy mornings when the air was filled with sunlit mist through which the sun and the blue sky were dimly visible yielded other and slightly different curves, always similar in form and characteristic of this state of the atmosphere (Fig. 8, *a*). Overcast skies gave distinctive forms (Fig. 8, *b*), notable for their general resemblance to certain curves obtained from the clear sky. The relations of these various types will be considered in a forth-coming paper. They are mentioned here only because of a certain bearing upon the theory.

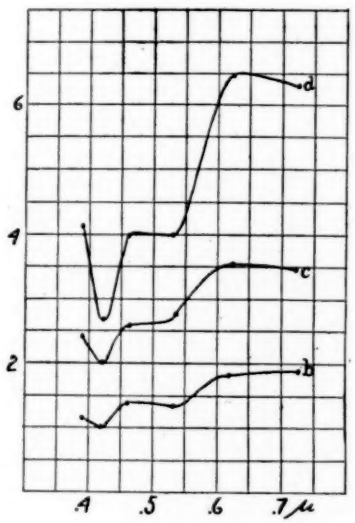


Fig. 5.

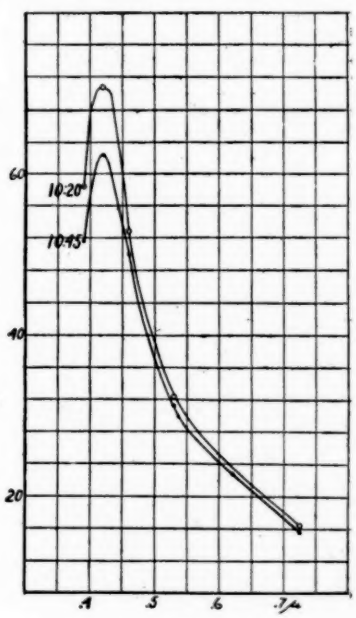


Fig. 6.

There is good reason to think certain features of the curves of ratios illustrated in Fig. 5 are due to the illumination of the sky by light reflected from the earth. The maximum at .625 μ and the minimum at .525 μ occur in all curves taken when the landscape is under direct sunlight. They are most marked in measurements made at stations in the open country, as at Taormina, Trafoi and Sterzing, less prominent in the winter skies at Biskra and Palermo and least of all in observations

at Vienna where the sky was always seen through a pall of smoke. Mist and over-cast skies, of which the curves in Fig. 8 (*a* and *b*) are typical, are devoid of these two selective features, as will be seen from the curves of ratios given in Fig. 9. Two of these examples, *B* and

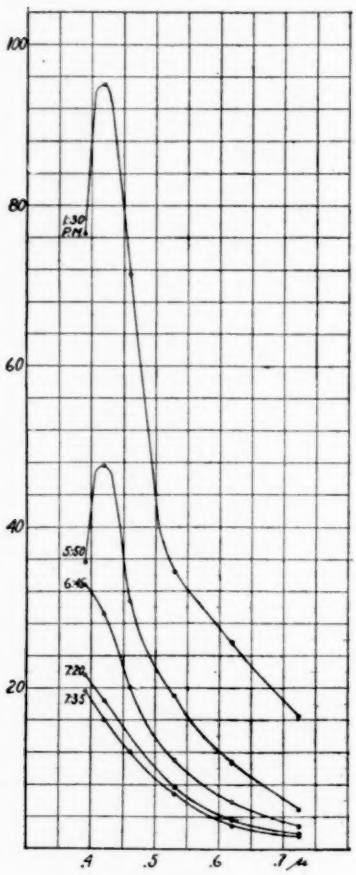


Fig. 7.

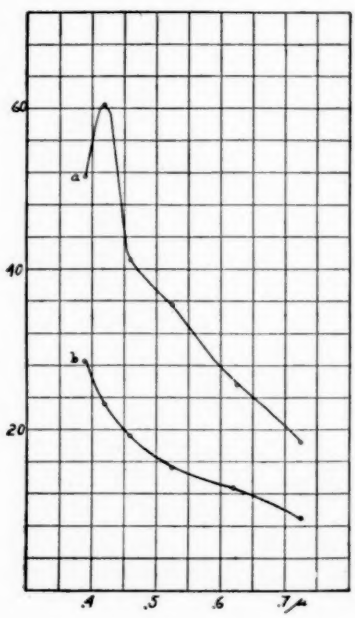


Fig. 8.

Z, are for fog, measured at Bebek on the Bosphorus and at Zell am See in Austria, and two, *V* and *T*, for clouded skies at Vienna and Taormina respectively when the landscape was untouched by sunlight. The absence of the features under consideration, and which are so obvious in Fig. 5, will be noted. These features are also missing in measurements taken at sea during bright weather. The fact that the region .525 μ corresponds to one of the strongest absorption bands of the spectrum of light transmitted by chlorophyl and .625 μ to the brighest portion of

that spectrum may be taken to indicate that presence of foliage modifies to a measurable extent the character of the light from the sky. In other words we have, when the landscape is sunlit, a weak chlorophyl spectrum superimposed upon the true spectrum of the light from the sky!

We have, therefore, in light reflected from the earth one of the causes of the deviation of many skies from the distribution of intensities to be expected from an ideal turbid medium illuminated only by direct sunlight. Reflection from cloud masses is often another source of illumination and by means of the spectrophotometer the selective character of such light, which closely resembles that from fog or mist, can readily be determined.

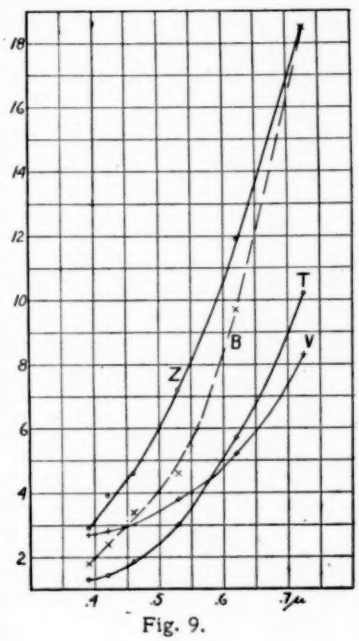


Fig. 9.

Inferences from the Polarization of the Sky.

Some of the strongest arguments for regarding the atmosphere as a turbid medium are derived from the study of the character of the polarization of skylight.

The phenomena described by Tyndall as the result of his study of artificial turbid media and his application of the same to the sky are confirmed and in a manner explained by observations with the spectrophotometer. Pernter[1] who made extended observations upon the light diffused by alcoholic solutions of mastic gum found the degree of polarization of the red, green and blue to vary in a remarkable manner according to the color of the emulsion. He found in general the light emitted at right angles to the illuminating beam to be less polarized the whiter the appearance of the medium — which is also true of the sky. For blue emulsions the green showed the greatest polarization, then the blue and then the red. For whiter emulsions the red was most strongly polarized and the effect diminished toward the violet. He found the same to be true of blue and whitish skies respectively.

In comparisons of the distribution of polarization in the spectrum of skylight from the zenith, taking the ratio of the brightness of the component polarized in the sun's vertical plane to that at right angles to the same, I obtained the results shown graphically in Fig. 10.

[1] Pernter, l. c.

It will be seen from the figure that the polarization of the sky is sometimes:

(*a*) Greatest in the violet.

(*b*) Greater in the green, yellow or blue than in the red or violet.

(*c*) Greatest in the red.

(*d*) Least in the middle of the spectrum.

(*e*) Nearly uniform throughout the visible spectrum.

The ideal turbid medium of Rayleigh would give complete polarization of all wave-lengths at an angle of 90°. If, with Pernter,[1] we consider that a medium may have this character for longer waves and yet reflect unpolarized light of shorter wave-length, the various cases noted above may be accounted for as follows:

(*a*) When the polarization increases towards the violet as in the ob-

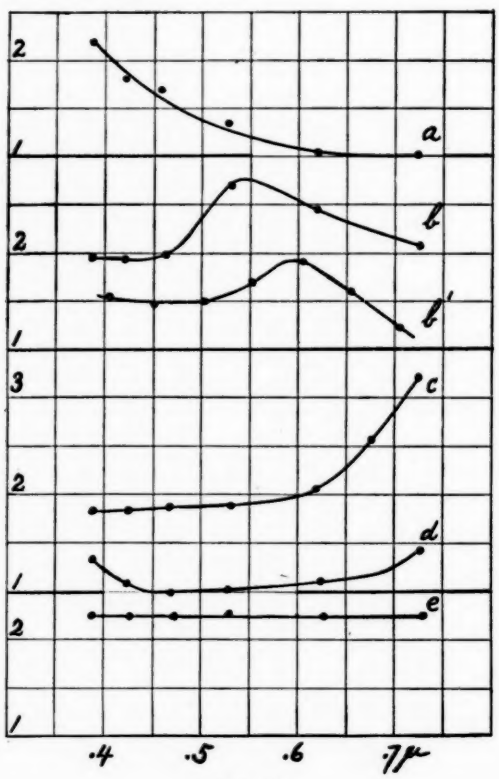


Fig. 10.

servations made at Biskra, February 23 (Fig. 10, *a*), we may suppose the light to come from an *ideal* medium with an admixture of coarser reflect-

[1] Pernter, l. c.

ing particles. Since light from the latter will be relatively weaker in the violet the percentage of polarized light will be greatest in that region and will diminish as we pass toward the red. The distribution of intensities in such a sky will obviously show greater relative strength at the red end of the spectrum than would the ideal sky.

(*b*) Observations made at Salzburg, July 5, 1907 (Fig. 10, *b*), also at sea on February 9 (Fig. 10, *b'*). The medium from which the light is derived may be a mixture of the *ideal* medium, with a medium ideal for green but not for violet, together with particles reflecting unpolarized light throughout the spectrum.

(*c*) Observations made at Chur on August 4 (Fig. 10, *c*). The *ideal* medium may be mixed with a medium ideal for red but not for green and the shorter wave-lengths, and also with coarser particles.

(*d*) Observations made at Biskra on February 24 (Fig. 10, *d*). It is possible that we have in this example a combination of the conditions producing *a* and *c*. Light from a region or layer of the atmosphere giving preponderance of polarization in the red may be considered as mingled with light from regions giving polarization chiefly in the violet.

(*e*) Case *e* offers greater difficulties. It might of course indicate an ideal sky but none of the skies for which this condition as to polarization was observed approached the ideal in relative intensity in the violet. The skies for which a uniform distribution of polarization was actually obtained were, indeed, very far from the ideal as to distribution of intensities. We may imagine as one of several combinations of circumstances which would produce this condition, a sky consisting of the ideal medium mingled with a coarser medium reflecting unpolarized light as in case (*a*) and that the preponderance of the polarized violet is removed by absorption of the light diffused by the ideal medium in passing through extended regions filled with the same. The change of composition would be analogous to that observed in fluorescent solutions of considerable concentration, where there is always a shift of the fluorescence band toward the infra-red. One may also imagine other combinations where the effects described under *b*, *c* and *d* happen to balance each other giving uniformity throughout the spectrum. Skies giving polarization curves of the types *b*, *b'* and *c* might obviously be expected to show the phenomenon designated by Tyndall as *residual blue*.

Evidence Concerning Other Factors in the Production of Skylight.

As has already been pointed out, the blue color of the air itself and a blue or violet due to fluorescence of ozone or other components of the atmosphere are to be regarded as possible factors in the production of the color of the sky. Data upon this subject are very incomplete and not

altogether conclusive. It is significant however that Crova in certain of his measurements, referred to in a previous paragraph, obtained an exponent much higher than that demanded by Rayleigh's theory. I find furthermore that all available measurements which give a near approach to the proper relation between the extreme red and the violet of the spectrum, namely, an increase of intensity of the violet which is inversely

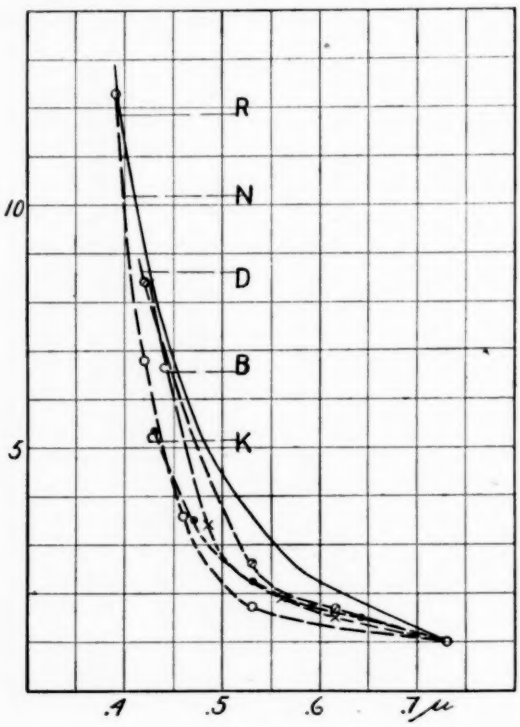


Fig. 11.

proportional to the fourth power of the wave-length, give values relatively much too small in the middle of the spectrum. This is true of the twilight and dawn curves obtained from my own measurements and likewise of the only set of measurements made by Bock in which the intensity of the violet approached the value corresponding to that of the ideal sky. While Miss Köttgen made no direct comparisons of sky and sun she measured both skylight and sunlight in terms of the Hefner lamp. Making use of her data one can compute the sky/sun ratios under the assumption that the sunlight at the time that the sun curve was taken was of the same quality as that during the comparison of skylight with the standard flame. I have made such a computation and find the resulting

curve to have the same peculiarity, that is to say, like the curve plotted from Bock's data and like my own curves there is marked relative weakness throughout the middle of the spectrum. This peculiarity could be readily explained by assuming a turbid medium containing particles too large to give the ideal sky but having a distinct blue color of its own due either to absorption, in accordance with Spring's theory, or it might be due to fluorescence in the violet end of the spectrum or to absorption and fluorescence combined. The nature of the departure of these curves from the ideal form, which is illustrated in Fig. 11, is quite consistent with and indeed explanatory of the occasional high values of the exponential factor found by Crova. In Fig. 11, R is the curve for the ideal turbid medium, N is one of the very few cases in which I obtained a relation between red and violet in accord with Rayleigh's theory. D is from my typical dawn curve, B and K are from the data of Bock and Köttgen respectively.

SUMMARY.

It has been my endeavor in this paper to show:

1. That while there is good reason for regarding the sky as a turbid medium, the experimental study of the spectrum of skylight affords evidence of a distribution of intensities which cannot be altogether accounted for by the assumption of an atmosphere conforming to Rayleigh's formula nor of a turbid medium containing coarser particles.

2. That the illumination of the atmosphere by selectively reflected light from the surface of the earth and from cloud masses and mist modifies the character of the light from the sky to an extent which while perhaps not readily discernible with the unaided eye is definite and unmistakable when the sky is studied with the spectrophotometer.

3. That the deviation of the observed distribution of intensities recorded by several investigators indicates a blue absorption color of the air or, since the preponderance in the violet appears to be variable in amount, the existence of fluorescence of some unstable factor of the atmosphere such as ozone or both.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY,
February, 1908.

MINUTES OF THE FORTY-FIRST MEETING.

THE spring meeting of the Physical Society was held in Washington, D. C., on Friday, April 24, and Saturday, April 25, 1908. President E. L. Nichols presided.

The Friday session was held at the Cosmos Club, and the Saturday sessions at the Bureau of Standards. At the close of the Saturday afternoon session, upon invitation of the director, the Society visited the new Geophysical Laboratory of the Carnegie Institution.

The secretary reported that the informal mail ballot on the question of increasing the annual dues showed 255 votes in favor of the increase and 32 against. Acting upon recommendation by the Council the Society thereupon voted to amend Article II. of the By-Laws by striking out the word "five" and inserting in its stead the word "six," the effect of the amendment being to increase the annual dues of members to six dollars.

The attention of the Physical Society was called to an International Electrical Congress which it is proposed to hold in London next October. It was suggested that the questions involved be fully discussed, previous to the meeting, by a joint committee representing the American Physical Society, the American Institute of Electrical Engineers, and the Electro-Chemical Society, in order that the delegates to be appointed by this Government should have the benefit of the opinions reached by American investigators who have been engaged in a study of the standard cell and the silver coulometer, as well as those who have given especial attention to the other questions involved in the selection and definition of the fundamental electrical units.

On motion the president was authorized to appoint such a committee, and Messrs. Bedell, Carhart, Guthe, Hulett, Rosa, Elihu Thomson, Webster, and Wolff were named by the president as members of the committee.

The following papers were presented:

What Proportion of the Earth's Magnetic Force in the United States is Due to a Potential? L. A. BAUER.

The Effect of Wave Form upon Magnetic Hysteresis. MORTON G. LLOYD.

The Influence of Terminal Apparatus on Telephonic Transmission. LOUIS COHEN.

What is the Most Important Portion of a Thermoelement? WALTER P. WHITE.

A Study of Photo-active Cells Containing a Fluorescent Electrolyte. PERCY HODGE.

A Photometer for the Measurement of the Rate of Decay of Gas Phosphorescence. C. C. TROWBRIDGE.

A Spectrophotometric Study of Kathodo-luminescence. EDWARD L. NICHOLS and ERNEST MERRITT.

A Study of the Thermo-luminescence of Balmain's Paint. (By title.) C. A. PIERCE.

Variation of the Penetrating Radiation. W. W. STRONG.

Specific Heat of some Calcium Chloride Solutions. H. C. DICKINSON and E. F. MUELLER.

The Application of the Ionization from Hot Bodies to Thermometric Work at High Temperatures. O. W. RICHARDSON.

Note on the Joule-Thomson Effect in Superheated Steam. H. N. DAVIS.

New Groups of Residual Rays in the Long Wave Spectrum. Preliminary Report. E. F. NICHOLS and W. S. Day.

Resonance Spectra of Sodium Vapor. R. W. WOOD.

Interference of Light in Laminæ of Chlorate of Potash. R. W. WOOD.

Experiments with the Lippmann Color Photograph. H. E. IVES.

The Relation of Light of Very Short Wave-length to some Vacuum Tube Phenomena. THEODORE LYMAN.

Additional Observations on the Selective Reflection of Salts of Oxygen Acids. LEIGHTON B. MORSE.

Optical Properties of Colloidal Solutions and Turbid Media in the Infra-red. B. J. SPENCE.

On Diffuse Reflection of Infra-red Energy. A. TROWBRIDGE.

Fundamental Questions Involved in the Selection of Definitions and Specifications of Electrical Units. S. W. STRATTON.

The Relative Merits of the Coulometer and Standard Cell from the Standpoint of their Use in Fixing the Values of the Fundamental Electrical Units. F. A. WOLFF.

The Infra-red Absorption and Reflection of Collodion. A. TROWBRIDGE.

The Absorption Spectrum of Neodymium in Mixed Solvents. JOHN A. ANDERSON.

The Remarkable Optical Properties of Carborundum. L. E. JEWELL.

Specific Heats at High Temperatures. (By title.) WALTER P. WHITE.

Preliminary Note on the Effect of Low Temperature on Optical Rotation. (By title.) F. A. MOLBY.

An Electrodeless Method for Measuring the Conductivity of Electrolytes. LOUIS COHEN.

Note on the Radioactivity of Ordinary Metals and on the Penetrating Radiation from the Earth. (By title.) J. C. MCLENNAN.

The Absorption and Reflecting Power of Calcite and Aragonite in the Infra-red as Dependent upon the Plane of Polarization of the Incident Rays. (By title.) R. E. NYSWANDER.

At the close of the meeting the society unanimously adopted a vote of thanks to the Bureau of Standards, the Geophysical Laboratory, the Cosmos Club, and the Philosophical Society of Washington, for the courtesy and hospitality extended to the society.

ERNEST MERRITT,
Secretary.

A NEW FORM OF INTERFEROMETER.[1]

BY C. W. CHAMBERLAIN.

THIS instrument is provided with three carriages, any one of which may be moved over a single bed plate by means of a slow motion screw. On the central carriage are mounted two $8 \times 25 \times 80$ millimeters plane parallel plates in contact with each other. Their outer faces are covered for 55 millimeters of their length with reflecting metallic surfaces, while the inner surface of one plate is provided for 25 millimeters or more of its length with a semi-transparent metallic film. A thin film of Canada balsam may be placed between the plates. On the end carriages are mounted mirrors $10 \times 25 \times 70$ millimeters with their reflecting surfaces facing the central plates and making equal but variable angles with them.

Light incident upon the semi-transparent film is reflected and transmitted to the end mirrors and then reflected many times between them and the silvered portions of the central plates. The reflected and transmitted beams are finally returned over their paths to the semi-transparent film where they are partly transmitted and reflected to the eye and are recombined and made to interfere.

By changing the angle between the end mirrors and the central plates interference fringes from the first to the twentieth order may be made to appear. The instrument is readily adjusted to bring fringes of several different orders into the field of view at the same time.

The following relationship exists between the movement of the central carriage and the number of interference fringes seen to cross the field of view.

Let β = angle between the central plates and the end mirrors.

x = movement of the central plates in a direction normal to their surfaces.

n = number of the order of the fringes, *i. e.*, n gives the number of times the ray is reflected from an end mirror.

f_n = number of fringes that pass the field of view when the nth order of fringes is used.

λ = wave-length of light employed.

$$x = \frac{f_n \lambda}{4 \cos\beta \cos n\beta \left\{ \frac{1}{\cos n\beta \cos (n-1)\beta} + \frac{1}{\cos (n-1)\beta \cos (n-2)\beta} + \frac{1}{\cos (n-2)\beta \cos (n-3)\beta} + \cdots \frac{1}{\cos\beta} \right\}}.$$

[1] Abstract of a paper presented at the New York meeting of the Physical Society. February 29, 1908.

The Relation of Light of Very Short Wave-Length to Some Vacuum Tube Phenomena.[1]

By Theodore Lyman.

SCHUMANN has observed that the radiation which comes from the neighborhood of the cathode in a vacuum tube is particularly rich in light of very short wave-length. The writer began the present investigation for the purpose of ascertaining if these most refrangible rays were confined entirely to the region near the negative electrode.

As a result of these experiments it may be stated that the positions of the sources of light of very short wave-lengths coincide with the places of luminosity in the vacuum tube. Thus the ozone test[2] shows some slight effect very near the cathode, little effect in the Crookes dark space, a maximum effect at the head of the negative glow, no effect in the Faraday dark space, a feeble effect throughout the length of the positive column, and a fairly well marked effect near the anode.

The latter half of the paper relates to the part played by light of very short wave-length in producing ionization within a discharge tube. That some kind of radiation acts to increase the conductivity in the electric discharge at low pressures has been proved by J. J. Thomson, and the effect has been attributed by him to the influence of the "Entladungsstrahlen" discovered by Wiedemann. One of the objects of the present paper is to show that in all probability the active agent in producing ionization is not a new form of radiation but light of wave-lengths shorte than λ 1,800.

The subject naturally leads to an inquiry into the nature of Entladungsstrahlen themselves. The writer points out that the phenomena attributed to this new agency are complicated by the action of light of very short wave-length to a far greater extent than had previously been supposed.

Jefferson Physical Laboratory,
Harvard University,
April 22, 1908.

A Photometer for the Measurement of the Rate of Decay of Gas Phosphorescence.[1]

By C. C. Trowbridge.

THE author described a new form of photometer designed for the purpose of measuring the rate of decay of luminosity of a phosphorescent gas. The photometer consists of a track 3.5 meters long, made of two brass rods under tension. On the track an electrically controlled carriage runs which carries the standard light. The standard light

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1908.

[2] Astrophysical Journal, March, 1908, p. 98.

can be moved away from a screen placed close to a tube containing the phosphorescent gas to points *A*, *B*, *C*, etc., on the photometer track. The illumination on the screen from the standard light is thus directly compared with the luminosity of the gas, and comparisons are made with the standard light at *A*, *B*, *C*, etc., as the gas fades. When a comparison is registered at *A*, the time recording key also releases the carriage carrying the standard light so that it moves by means of weights until stopped at *B*, ready for the next comparison. Seven readings can be

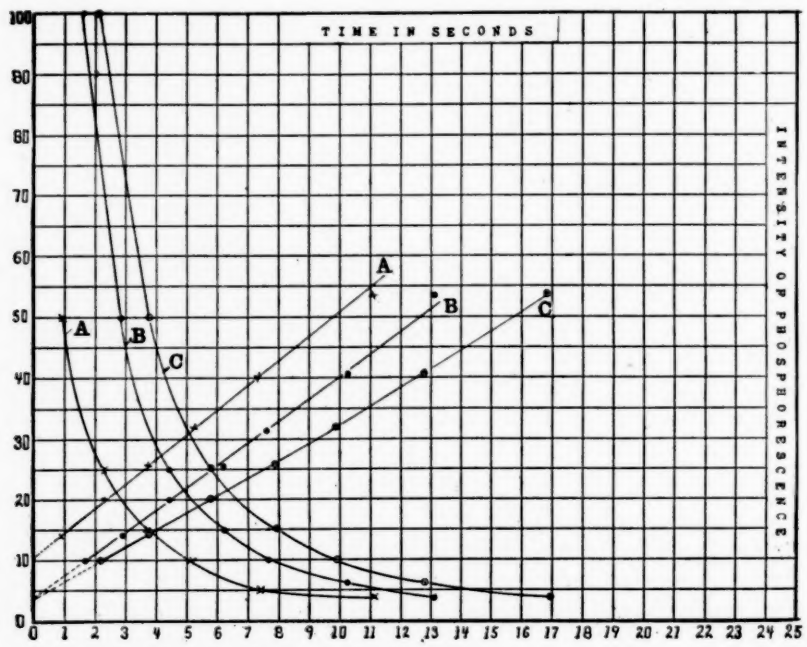


Fig. 1. Decay of phosphorescence in air; *A* at 0.14 mm. gas pressure, *B* at 0.227 mm. pressure, *C* at 0.222 mm. pressure. Curves *B* and *C* show different rates of decay at approximately the same gas pressure, due to changes in the condition of the rarefied gas.

made within ten seconds, giving a variation of from one half to one twenty-fifth the original intensity of the phosphorescent gas. The entire apparatus is operated electrically, time being registered on a chronograph.

By means of this photometer the law of the rate of decay of phosphorescence for gases has been found; in this case, for air at from 0.1 to 0.4 mm. gas pressure, the expression is the same as that for the decay of phosphorescent solids, found by Nichols and Merritt.[1]

$$I = \frac{1}{(a + bt)^2}$$

[1] PHYSICAL REVIEW, XXII., 5, May, 1906.

If the reciprocal of the square roots of the intensities are plotted with the corresponding times, a straight line is obtained. The points representing the observation of one decay of the phosphorescent gas are sufficient to demonstrate the law as shown by the accompanying curves. These curves shown in Fig. 1 are at different gas pressures, other conditions being the same. It appears that the initial intensities of the glows diminish very rapidly with decreasing gas pressure. An application of the law to the fading of the light of a body of phosphorescent gas as great in size as a long enduring meteor train shows that the light of the self-luminous meteor train can be explained on the assumption that it is a gas phosphorescence, although the train may be visible for thirty minutes. A certain brightening of the sky around the radiant point at the time of meteor showers which has been called the "auroral light" is also explained by the application of the same law. In the latter case it is probable that the feeble phosphorescing of many trains has combined to give a pale glow in the region of the heavens through which the shower was taking place.

The determination of the law for the decay of the phosphoresence of air, greatly strengthens the hypothesis that the meteor train is a gas phosphorescence; and also, if the meteor train is the same as this gaseous afterglow which can be produced in the laboratory, then a phenomenon precisely similar to the "auroral light" referred to above should be expected at every great meteor shower.

Experiments with the Lippmann Color Photograph.[1]

By Herbert E. Ives.

THE colors in this process are due to reflection from laminæ of silver deposited in the loops of the standing wave system formed by reflection of the incident light by a mercury surface in contact with the transparent photographic film. Theoretically the purity of the reflected colors should increase with the thickness of the film. In practice very thin films are used because the laminæ are formed to but a short distance and the absorption of light by them makes but few effective. The reflected colors are far from pure. The necessity for using a mercury trough has always been a disadvantage of the process. The colors of natural objects have been difficult of reproduction because the standing wave system is shallow and unduly subject to errors of exposure and development.

The present experiments show that the non-formation of laminæ at a distance from the surface of the film is due to the kind of developer ordinarily used, pyrogallic acid. This is brought out by sections made of the films, which wetted so as to swell are examined with the microscope. It is found that the photographic action extends through the thickest films

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1908.

practicable to flow. By using other developers, such as hydroquinone, even action throughout the film results. If the developed image is then bleached with mercuric chloride a transparent deposit is obtained, and the reflected light consists of a spectrum band of only a few A.U. in width, the purity increasing with thickness of film.

A substitute for the mercury mirror has been found. Celluloid varnish is flowed on silvered glass; on drying the celluloid and silver strip off together, this flexible mirror is then laid on a wet Lippmann film and allowed to dry. Exposure is made as with ordinary dry plates, the celluloid stripped off and film developed.

Because of the difficulty experienced in securing photographs of natural objects an application of the process to three-color photography was tried. For this fairly pure spectrum colors are needed and the Lippmann film is eminently fitted to give them. Pictures are made similar to the Joly picture, — alternating lines of red, green and blue, secured by successive exposure behind a line-screen to monochromatic lights.

VARIATION OF THE PENETRATING RADIATION.[1]

BY W. W. STRONG.

AN electroscope of the Wilson type was placed in screens of water, iron and lead. It was found that the rate of leak in the vessel under these conditions was constant. The same electroscope unscreened, however, shows very considerable changes in the rate of leak. By covering the electroscope with a thin cap of blackened wood, the effects of easily absorbable external radiations are eliminated. Under these conditions one gets the effects of the so-called penetrating radiation and temperature only. Under these conditions if the rate of leak is at any time the same as for the electroscope screened with iron or lead, it indicates that the penetrating radiation is zero. A few results will now be given, the rate of leak being the average over the period of time indicated.

Time.	Rate of Leak, Scale Divisions per Second.	Per Cent. Penetrating Radiation.
1908, March 26, 8 hrs. 50 min. A. M.		
5 " 20 " P. M.	.000014	40
March 27, 8 " A. M.	.000016	60
5 " 40 " P. M.	.0000155	55
March 28, 10 " 5 " A. M.	.000013	30
Showers, 5 " 5 " P. M.	.000010	0
March 29, 2 " 25 " P. M.	.000011	10
April 4, 8 " 15 " A. M.		
4 " 10 " P. M.	.000010	0
April 5, 1 " 30 " P. M.	.0000106	6
April 6, 10 " 15 " A. M.	.000014	40

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24-25, 1908.

During March 28 there were showers. In general it has been found that during rains or snows the penetrating radiation is much smaller than usual. On April 3 the weather changed from being warm to being very cold. Under these cyclonic conditions of the winds, air from the colder and upper strata of the atmosphere flows towards the surface. It was found in this case that the penetrating radiation was practically of zero value. This would indicate that this air contained very little radioactive material — at least very little of the products that are the sources of penetrating γ rays.

JOHNS HOPKINS UNIVERSITY.

THE SPECIFIC HEAT OF SOME CALCIUM CHLORIDE SOLUTIONS.[1]

BY H. C. DICKINSON AND E. F. MUELLER.

A DETERMINATION of the specific heat of some calcium chloride solutions was first undertaken chiefly in the interests of the refrigeration industry to which it is of considerable importance.

A calorimeter of the continuous flow type was designed with a view to working at temperatures as low as $-35°$ C. and making determinations of specific heat in a temperature interval of from 5° to 10° with an accuracy of approximately 0.1 per cent. The calorimeter consists of a heavy copper vessel of about one liter capacity containing some two meters of copper tubing wound with resistance wire and bent into a spiral, a second coil of resistance wire and a stirrer. Since it was not necessary to know the water equivalent with accuracy, kerosene was used for filling, with the heating coils directly immersed in it.

A stream of calcium chloride brine from a cold reservoir is drawn through the copper coil under a constant head and the temperature of the calorimeter maintained constant by supplying energy electrically. The use of two heating coils, one of which is in close contact with the brine coil and the other separated from it, makes it possible to choose within rather wide limits all the temperature conditions and the rate of flow, by adjusting the ratio of energy supplied by the two coils. The calorimeter proper is held within a larger closed vessel by heat-insulating supports and kept at the same constant temperature as this vessel by observing a differential thermo-couple. By this method radiation and conduction and water equivalent corrections are almost negligible. The energy supplied by the stirrer is determined by separate experiments at different speeds.

Measurements to be taken are as follows: (1) Time (usually ten minute intervals) observed on a carefully regulated watch, (2) weight of brine, (3) energy supplied electrically, by potentiometer with standard

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1908.

shunt and volt box, (4) temperature difference between inlet and outlet of the brine coil, measured by differential platinum resistance thermometers (described in the June, 1907, PHYSICAL REVIEW), (5) inlet temperature of brine, measured by one of the resistance thermometers. The rate of stirring and small changes in the temperature of the calorimeter are also observed and corrections made, seldom amounting to one per cent. of the energy used.

The following results are only preliminary as the investigation is still in progress. Observations have been made on one of the purest and most generally used commercial calcium chlorides with results as follows, with a probable error not exceeding 0.1 per cent. unless possibly for the most dense brine at the lowest temperatures.

Specific gravity 1.26		Specific heat $.666 + .00064t$	$(-35°$ to $15°)$
" " 1.20		" " $.708 + .00064t$	$(-20°$ " $15°)$
" " 1.14		" " $.772 + .00064t$	$(-10°$ " $15°)$
" " 1.07		" " $.869 + .00057t$	$(0°$ " $15°)$

A few determinations have also been made with pure water as a check on the method and the value found for the specific heat at 15 was .9995 with a negative correction for temperature but the magnitude of this correction was not carefully determined. These results are all reduced to a value of 4.196 for the 15° calorie in electrical units based on the international ohm and volt.

ABSORPTION SPECTRUM OF NEODYMIUM IN MIXED SOLVENTS.[1]

BY JOHN A. ANDERSON.

WHEN pure, anhydrous neodymium chloride is dissolved in water it gives a very characteristic absorption spectrum for which Beer's law holds accurately unless the solution is nearly saturated. If the anhydrous salt is dissolved in methyl or ethyl alcohol or acetone the same statement is true, but the absorption spectrum is different from that of the aqueous solution, most of the bands having apparently shifted somewhat towards the longer wave-lengths in accordance with Kundt's law; also, the structure of the bands is generally different in different solvents. It was thought to be of interest to try the effect of using mixtures of water and one of the non-aqueous solvents, keeping the concentration of the dissolved substance constant but varying the proportion of one of the solvents to the other in the mixture. It was found that the spectrum of neodymium chloride *does not change appreciably* when the proportion of methyl or ethyl alcohol to water was varied from 0 to 85 per cent., and that when the proportion was varied from 85 per cent. to 100 per cent. *there is not a gradual shift of the bands* but that *two*

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1908.

sets of bands coexist; the bands characteristic of the aqueous solution disappearing gradually, while those due to the alcoholic solution increase in intensity.

The composition of the mixture in which the two sets of bands have about equal intensity for a half-normal solution was found to be roughly 8 per cent. water and 92 per cent. alcohol. For a quarter normal solution it was roughly 5 per cent. water and 95 per cent. alcohol. In both cases, therefore, the two sets of bands have equal intensity when the mixture contains about ten molecules of water to each molecule of neodymium chloride.

The results indicate that the absorption spectrum of the aqueous solution is due to some definite hydrate which is always formed provided there is sufficient water present. If the amount of water is not sufficient then some of the neodymium chloride will combine with the alcohol forming perhaps some definite alcoholate having an absorption spectrum different from that of the hydrate.

This work is a part of an investigation on the absorption spectra of solutions carried out during the present year by Professor H. C. Jones and the writer.

JOHNS HOPKINS UNIVERSITY,
April 9, 1908.

OPTICAL PROPERTIES OF COLLOIDAL SOLUTIONS AND TURBID MEDIA IN THE INFRA-RED.[1]

BY B. J. SPENCE.

A NUMBER of theoretical and experimental papers have appeared from time to time dealing with the optical properties of colloidal solutions and turbid media. Among the more recent are those of Müller,[2] whose paper is of an experimental nature, and the article of Mie[3] which is largely theoretical.

Among the earlier memoirs is one by Garnett,[4] which has an important bearing upon the investigation. The analysis given by Garnett was extended by the present writer, so that it is possible to make use of it by him in investigating the colloidal solutions.

In Garnett's analysis, he develops the following equation:

$$\epsilon' = n'(1 - K') = 1 + \frac{3M\dfrac{H^2 - 1}{H^2 + 2}}{1 - M\dfrac{H^2 - 1}{H^2 + 1}}$$

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1908.

[2] Ann. der Phys., 24, p. 1, 1907.

[3] Ann. der Phys., 25, p. 337, 1908.

[4] Phil. Trans., A, 204–205, 1904–1905.

where n' = refractive index of the colloidal solution,
K' = absorption coefficient of the colloidal solution,
M = volume of metal per c.c. of supporting medium,
$H = n(1 - iK)$,
n = refractive index of the metal,
K = absorption coefficient of the metal.

In the above analysis it is assumed that the metallic particles are spherical in shape and that there are many to the wave-length.

The work of Ehrenhaft[1] and Zsigmondy and Siedentopf,[2] has shown that these suspended particles are spherical in shape and of the order of magnitude of 10^{-5} cm. One important theory in Garnett's work is the fact that the optical properties seem to be independent of the number of particles in unit volume.

Garnett's analysis was so developed as to account for an absorbing supporting medium and to give value for the optical constant n of the metals. The equations are the following:

$$n^2 = \frac{4\beta(\nu^2 A - \nu^2 g K) + (2\nu^2 g A + 3\nu^2 K)}{2\{\beta(A^2 + 4K^2 g) - (Ag + 4K^2 g)\}} - \sqrt{\left\{\frac{4\beta(\nu^2 A - \nu^2 g K) + (2\nu^2 g H + 3\nu^2 K)}{2\{\beta(A^2 + 4K^2 g - (Ag + 4K^2 g)\}}\right\}^2 - \frac{2\nu^4(g + 2\beta)}{\beta(A^2 + 4K^2) - (Ag + 4K^2 g)}}$$

where

$$\beta = \frac{-g}{3\mu} + \sqrt{\frac{g^2}{9\mu^2} + \frac{n'^2 K'^2}{9\mu^2 \nu^2}}$$

and ν = refractive index of the supporting medium,
g = absorption coefficient of the supporting medium,
$A = K^2 - 1$.

The general deduction from these equations is, first, the absorption of the colloidal solutions is directly proportional to the relative volume μ, or the concentration; second, that the value of n is independent of the supporting medium, n being what is usually defined as the refractive index of the metals.

These conclusions were tested for platinum, gold and silver colloids, and it was found that the values of n obtained were independent of the absorbing medium, that the absorption was directly proportional to the concentration. The values of n do not agree with those given by Drude for the wave-length 5.89×10^{-5} cm.

[1] Sitz. ber. Akad. Wiss. Wien., 114, II. A, 1905.
[2] Liebig's Ann., CCCI., p. 29, 1898.

The work was performed with a large spectro-bolometer provided with a rock salt prism 16 cm. in height and a face width of about 5.5 cm. The colloidal solutions were electrically prepared, both in water and ethyl malonate.

The values of n for gold, silver, and platinum lie upon a smooth dispersion curve, and were carried to a wave-length of 20×10^{-5} cm. The range of values is somewhat limited due to the strong absorption of water and ethyl malonate after it reaches a wave-length of 19×10^{-5} cm. A typical turbid medium composed of non-conducting particles was made of gum mastic and its properties studied. It showed an increased transparency for the longer wave-lengths as did the colloidal solutions. The absorption was found not to vary directly as the concentration, but as some other linear function. It remains yet to investigte whether turbid media (composed of non-conducting particles) obey the Rayleigh formulas, where the energy transmitted varies as the λ^{-4}.

The above is submitted as a preliminary report of work which is still in progress, and nearing its completion.

The Effect of Wave Form upon Magnetic Hysteresis.[1]

By Morton G. Lloyd.

MANY previous workers have sought to measure the energy expended in hysteresis with different frequencies and different forms of wave, but with results in such disagreement that the question may be considered as unsettled as yet. The author, with Mr. J. V. S. Fisher, has made measurements of the total iron losses with alternating magnetization by plotting curves between the instantaneous values of magnetizing current and magnetic flux. The apparatus used for this purpose has been described in a paper already published.[2]

The loops so obtained represent the total energy due to both hysteresis and eddy currents, and the value of the hysteresis alone cannot be accurately determined.

The wattmeter method has consequently been used to measure the total iron losses, and a separation of the hysteresis and eddy current components effected by using two frequencies and applying the modified form of the Steinmetz formula

$$W = anB^x + bn^2B^2f^2$$

where W is the power expended, n the frequency, B the maximum value of the flux density, a and b constants of the material, and f the form factor of the electromotive force induced in a coil enclosing the flux. The form factor is measured by means of the apparatus described in the

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1908.

[2] Lloyd and Fisher, Bull. Bureau of Standards, 4, p. 467, 1908.

article cited above, which also serves to determine the shape of the wave of magnetic flux and to fix the value of the maximum flux density. The form factor is altered by introducing resistance in the magnetizing circuit, or by introducing the third harmonic into the E.M.F. by means of a special set of generators. The change in eddy current loss with form factor can be computed, and the change in total loss is measured. If these are not equal, there must also be a change in hysteresis. The samples experimented upon were in the form of rings, made up by using sheet iron or iron wire. The results show that if there be any change in the hysteresis, with change of wave form, when B is kept constant, it is very small.

ADDITIONAL OBSERVATIONS ON THE SELECTIVE REFLECTION OF SALTS ON OXYGEN ACIDS.[1]

BY LEIGHTON B. MORSE.

IN a previous paper[2] it was shown that in general the bands of selective reflection, three and only three of which were found between 4 μ and 15 μ in each of eight simple carbonates with bivalent bases, shifted toward longer wave-lengths as the atomic weight of the base was increased, and further that this displacement was roughly proportional to the change in the atomic weight of the base.

The data obtainable on the first reflection bands of simple nitrates and sulphates were in agreement with the carbonates. Only crystalline solids free from water of crystallization, with simple elements as bases, were considered and salts having bases with the same valence as the acid radical were selected.

Since we know that the positions of reflection bands in salts of a given acid are influenced by the atomic weight of the base, when comparing the wave-lengths of bands of selective reflection characteristic of the different acid radicals it is necessary to eliminate as far as possible the effect of the base. The nearest approach to this was obtained by selecting salts of potassium for the monovalent acids and of calcium for the bivalent acids (atomic weight K = 39.15, Ca = 40.1).

At the time of writing the previous paper only carbonates had been examined, but combining the writer's data on $CaCO_3$ with the data of other observers[3] on KNO_3, $CaSO_4$, and $MgSiO_3$ (there were no data on $CaSiO_3$ and $MgSiO_3$ was the best substitute obtainable), it was found that an approximate linear relation existed between the wave-lengths of the first reflection bands and the weights of the acid-forming elements combined

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1908.

[2] Morse, PHYSICAL REVIEW, 25, p. 500, 1907.

[3] Coblentz, Invest. of Infra-red Spectra, 1906, and Pfund, Astrophys. Jour., 24, p. 39, 1906.

with a given weight of oxygen (48 grams was taken as in the carbonates). Making allowance for magnesium being lighter than calcium, it seemed that the approximate linear relation found could hardly be accidental. The tentative hypothesis was made "that the oxygen atom is the one chiefly responsible for the marked reflection observed."

A number of salts with oxygen acid radicals were examined which, if the supposed linear relation held, might be expected to give bands corresponding to the first band in carbonates, in the region of the spectrum for which a rock salt prism is transparent. Thus the reflection of one or more salts of ten different oxygen acids have been examined between 4 μ and 15 μ including $CaCO_3$, KNO_3, $AgNO_3$, $CaSO_4$, $KClO_4$, $CaSiO_3$, $KClO_3$, $PbCrO_4$, $KMnO_4$, and $CaTiO_3$. Nine of these have a weight of the acid-forming element less than the weight of the oxygen with which it is combined and without exception the potassium and calcium salts have their first bands at wave-lengths not only in the order of the weights combined with a given weight of oxygen, but the relation between the wave-length of the band and the weight of the acid-forming element combined with 48 grams of oxygen is roughly a linear one. The reflection curves of $AgNO_3$ and $PbCrO_4$ indicate that KNO_3 and $CaCrO_4$, which could not be directly examined because the former is highly deliquescent and the latter contains water of crystallization, have bands not far from the line drawn through the first bands of the other potassium and calcium salts.

Wollastonite, $CaSiO_3$, has a first band at the calculated wave-length 9.2 μ and beside this has a broad complex band toward the long waves from the first, but not far enough to fit in with the second region band found in the carbonates and found now for the first time in potassium and silver nitrates and in calcium sulphate. In perovskite, $CaTiO_3$, we have the largest weight combined with the given weight of oxygen in the acid radical (atomic weight Ti = 48.1, O_3 = 48). Its first band lies further toward the long waves than was predicted.

The values found for the wave-lengths of the first reflection bands had in most cases been calculated to within a few per cent. The second bands found in $CaCO_3$, KNO_3, and $CaSO_4$ seem to be related to each other. The $AgNO_3$ surface showed a low broad first band and it was impossible to determine whether or not the second band was present. The prediction of the second band in the other substances was beyond the sulphate band found at 14.5 + μ and could not be found, if present, with the rock salt prism used.

The substances examined include salts of all the common monobasic and dibasic oxygen acids obtainable in a suitable form, in which the weight of the acid-forming element is not greater than the weight of the oxygen with which it is combined, and which may be represented by the

general formula MAO_n. It must be kept[1] clearly in mind however that present data do not form any reasonable basis for assuming that all the reflection bands in even the simpler oxygen acids are connected with each other by such a simple relation as that found to hold roughly for the first bands, and which may be found to hold also for the second bands in the salts examined.

NEW GROUPS OF RESIDUAL RAYS IN THE LONG-WAVE SPECTRUM.[2]

BY E. F. NICHOLS AND WM. S. DAY.

THE apparatus used consisted of a number of Nernst glowers, usually five, as the source of radiation, a fine wire transmission grating, a reflecting spectrometer, and a Nichols radiometer, all enclosed in a glass case from which water-vapor was excluded. The mean wave-length of the residual rays after five successive reflections from polished rock-salt surfaces wa smeasured and found to be $\lambda = 52.3\,\mu$, somewhat larger than $51.2\,\mu$ found in 1898 by Rubens and Aschkinass. Residual rays were also found after five successive reflections from polished surfaces of the following substances, the wave-length of maximum energy in the diffraction spectrum of the first order being given in each case:

Ammonium chloride,	$\lambda = 51.4\,\mu$
Witherite (barium carbonate),	$\lambda = 46.5\,\mu$
Strontianite (strontium carbonate),	$\lambda = 43.2\,\mu$

As the radiometer had a thin quartz window, these wave-lengths are subject to revision because the changing transparency of quartz in this part of the spectrum would tend to shift the maximum energy observed to the long-wave side.

It should be noticed that the wave-lengths of the three known groups of residual rays from chlorides — potassium chloride, sodium chloride, and ammonium chloride, $61.1\,\mu$, $52.3\,\mu$, $51.4\,\mu$, while not strictly proportional, lie in the order of the atomic weights of their respective bases, 38.8, 22.9, 18. The same rule holds for the residual rays from the carbonates of barium and strontium, the heavier base giving the longer wave-length.

NOTE ON THE RADIOACTIVITY OF ORDINARY METALS AND ON THE PENETRATING RADIATION FROM THE EARTH.[2]

BY J. C. MCLENNAN.

IN a paper in the Phil. Mag., December, 1907, the writer described some experiments made by him on the conductivity of air confined in metallic cylinders, 60 cm. long and 24 cm. in diameter, which were

[1] Morse, Astrophys. Jour., 26, p. 241, 1907.

[2] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24-25, 1908.

made of lead, of zinc, and of aluminium. With the zinc and aluminium cylinders carefully cleaned, a conductivity was obtained for the enclosed air, which on reduction gave the value 15 for q, the number of ions generated in the air per c.c. per second.

With lead cylinders which were investigated more extensively than those of other metals, the conductivity exhibited wide variations, and values were obtained which ranged from 160 to 23 ions per c.c. per second.

During the past eight months experiments on the conductivity of air confined in metallic vessels have been continued in the Physical Laboratory at Toronto by Mr. C. S. Wright, and he has now obtained under normal conditions with a particular lead cylinder of the dimensions given above, a conductivity corresponding to the production of 15.3 ions per c.c. per second. With zinc and aluminium cylinders the lowest conductivities obtained by him as yet give respectively the values 13.4 and 12.5 ions per c.c. per second for q.

With gamma rays of the same intensity from radium traversing in turn the three cylinders of lead, zinc, and aluminium, which gave the values for q of 15.3, 13.4 and 12.5 respectively, the relative values of the impressed conductivities were found to be 14.00, 11.4 and 10.00. These relative values, it may be added, were found to be the same with gamma rays of all intensities. From the difference exhibited between these relative values and the numbers found for q for these same cylinders, it is clear that the whole of the conductivities obtained with them under normal conditions cannot be ascribed to a penetrating radiation existing at the surface of the earth and to a secondary radiation excited by it at the walls of the receivers.

With a view to ascertaining what portion of the conductivity obtained with each cylinder could be ascribed to the penetrating radiation and to the secondary radiation excited by it, a series of measurements was made on the conductivity of the air in the three cylinders in and about the neighborhood of Toronto. The results of these measurements are recorded in the following table.

The numbers obtained for q at station 2 it will be seen appear to be the lowest hitherto recorded under any circumstances for the ionization of air in closed vessels measured at normal pressure and temperature.

The average value obtained for q with the lead cylinder in the experiments over the surface of the water of Lake Ontario, as the table shows, was 9 ions per c.c. per second. The difference between this number and that obtained at station 10 in the laboratory, viz., 6.3 ions per c.c. per second, would therefore correspond to the conductivity impressed upon the air by a penetrating radiation which was present in the laboratory and by the secondary radiation necessarily accompanying it, but

which was entirely absent from the space in the open above the surface of the lake. The water of the lake would then appear to act as a screen for a penetrating radiation issuing from the earth. Some investigators, notably Strong, Phys. Zeit., February 15, 1908, have suggested that the atmosphere was the source of the penetrating radiation known to exist at the surface of the earth, but these results, coupled with the values obtained for the ionization at Station 8 on the University tower, constitute strong evidence against the validity of that view.

TABLE I.

Table of Conductivities.

Observation Station.		Remarks.	Value of q, the Number of Ions Generated per c.c. per Second.		
No.	Location.		Lead.	Zinc.	Aluminium.
1.	The ice on Toronto Bay, 100 meters from the Yacht Club Wharf.	Water, 10 meters deep. Ice, 30 cm. thick.	9 0		
2.	The ice near Canoe Club Wharf, Toronto Bay.	Water, 5.6 meters deep. Ice, 30 cm. thick.	8.6	6.0	6.55
3.	The ice on Grenadier Pond, an inlet of Lake Ontario. Station "a."	Water, 2.5 meters deep. Ice, 30 cm. thick.	9.2		
4.	The ice on Grenadier Pond. Station "b."	Water, 3.5 meters deep. Ice, 30 cm. thick.	9.0		
5.	At the shore of Grenadier Pond. Station "c."		9.1		
6.	On a sand hill overlooking Grenadier Pond.	Height of hill about 50 meters. Distance from shore, 100 meters.	9.3		
7.	University lawn.	Clay soil, sodded, frozen and covered with ice and snow, 20 cm. deep.	11.2		
8.	University tower.	26 meters high.	11.4		
9.	In the open on the ground in the rear of the new physical laboratory.	Frozen clay, recently overturned covered with 10 cm. of ice and snow.	13.2	11.1	10.4
10.	A room in the basement of the new physical laboratory.	As the building is new it was supposed to be free from any radioactive contamination.	15.3	13.4	12.5

Confirmative evidence of the existence of this difference in the conductivities of air when contained in a closed vessel measured on land and on the surface of the water of Lake Ontario was obtained in some measurements made in September last. In that month, a series of observations was made in the laboratory on the conductivity of air in a lead cylinder, and the average value for q with this receiver was found to be 41.7 ions per c.c. per second. Measurements were also made with this same receiver on board the steamer "Corona" during one of her passages over Lake Ontario, and an average value for q of 35.8 ions per c.c. per second was found. A third set of measurements was then made on land in the open on the south side of the lake at a number of points between Queenston and Niagara Falls, and an average value of 42.6 was found for q. Here again it will be seen that a difference of approximately 6 ions existed between the values found for q on the water and those found for this quantity on the land. It is interesting to note in this connection that very little variation was obtained in the conductivity in the measurements made at different points during the passage of the boat, although the depth of the water at the wharf was only some 6 meters, while at the middle of the lake it was over 150 meters deep.

The experiments made at Stations 5 and 6 are also of special interest, as the conductivity obtained at these points was practically the same as that obtained in the experiments on the surface of the lake, which shows that the sand was entirely free from the radioactive substances which were probably present in the clays and rocks at other points of observation. Some additional evidence of this freedom from radioactive substances was obtained from a further set of observations made in December last at Ward's Island, which is a low-lying sand bar forming part of the boundary of Toronto Bay. There the conductivity of air in a lead cylinder was found to be the same when measured on the island as when measured on the water of the adjoining bay.

Some years ago the writer made an examination of the water of Lake Ontario and was unable to detect in it any measurable amount of radium emanation. From the lack of emanation in this water, and from the uniformity existing in the values obtained for q on its surface for all depths, it would appear probable that the water entirely cuts off any radiation coming from the soil or rocks beneath it.

In support of this view some experiments made on the absorption by this water of the gamma rays from radium may be cited.

A capsule containing thirty milligrams of radium was hermetically sealed in a glass tube which was then enclosed in a tube of brass whose walls were 1 cm. in thickness. This tube was then laid on the ice on Grenadier Pond, and the ionization cylinder supported on a table 113 cm. high was placed over it, and the conductivity due to the radium

measured. A hole was then made in the ice and the tube containing the radium lowered to different depths, the ionization in the cylinder at each depth being measured. The values found for Q the number of ions generated per c.c. per second by the radiation from the radium for the various depths are given in Table II.

TABLE II.

Depth of Water Over Tube Containing Radium.	Q
0 meters.	4,485.0
0.5 "	447.2
1 "	16.11
2 "	.69
3.65 "	.62

From this it will be seen, after allowing for a variation in the intensity of the radiation due to the increased distance from the measuring chamber, that the intensity of the radiation reaching the ionization cylinder after traversing 3.65 meters of water, was not more than one part in 500 of its intensity when the radium was on the surface of the ice. From these numbers it would appear, therefore, that if the water of the lake contributed itself no penetrating radiation, the amount which could get through the water to the surface from the earth beneath would form a negligible proportion of that issuing from the different rock and soil surfaces on land.

On the basis of this argument it follows that the ionizations given in Table I. for observation Station 2 may be taken to represent the conductivities impressed upon the air either by intrinsic radiations issuing from the metals of the receivers themselves, or else by radiations from active impurities still remaining in them.

The difference between the numbers for this station and those for station 10 are, as will be seen from the table for the different cylinders, as follows: Lead, 6.7; zinc, 7.4; aluminium, 5.95. These numbers, as is evident, are not proportional to the relative ionizations impressed on the air in the three cylinders by the penetrating rays from radium. The number for zinc, especially, exhibits a considerable discrepancy, and further measurements should be made to ascertain the cause of it.

Considered as a whole the experiments described above are interesting from the light which they throw on the question of radioactivity of metals and substances generally. The values obtained for q for the three cylinders at Station 2 differ from each other but little. They are moreover of the order of magnitude of effects which might easily be accounted for by active impurities in the metals, for differences as large as these values of q may be easily obtained with cylinders made from different samples

of almost any metal selected at random. Considering also the difference in the atomic weights of the three substances, aluminium, zinc, and lead, and having in mind that radioactivity is a property associated with atomic structure, it would seem that if these metals could be obtained entirely free from active impurities, and the conductivity of air contained in vessels made from them studied, it would be found, if the observations were carried out under conditions or in places where no ionization was possible from penetrating radiations arising from external sources, to drop to a very low value if it did not entirely vanish.

The experiments described in this note were made with one of C. T. R. Wilson's latest type of gold-leaf electrometers, which was found, on account of its portability, and of the facility and exactness with which readings could be made with it, to be most admirably suited to the purposes of the investigation.

PHYSICAL LABORATORY,
UNIVERSITY OF TORONTO,
March 30, 1908.

THE INFLUENCE OF TERMINAL APPARATUS ON TELEPHONIC TRANSMISSION.[1]

BY LOUIS COHEN.

THE problem of telephonic transmission has been very ably treated by several investigators. One has to examine only the collected papers of Dr. Oliver Heaviside, and the two papers on the "Propagation of Electrical Waves" by Professor M. I. Pupin, and he will find a discussion on almost every phase of the problem. But while there is very little that one could add to the mathematical treatment of the problem, yet there is one point in connection with this problem "The Influence of Terminal Apparatus on Telephonic Transmission" which has not been given sufficient attention, and I trust a brief discussion of this phase of the problem will be of some interest.

If L, R, C denote the inductance, resistance and capacity of the line per unit length; X the current, V the potential at any point on the line, then the equation of propagation will be as follows:

$$L\frac{d^2x}{dt^2} + R\frac{dx}{dt} = \frac{1}{c}\frac{d^2x}{ds^2}$$

and we also have the relation

$$C\frac{dv}{dt} = -\frac{dx}{ds}.$$

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1908.

At the terminals the following relations will obtain

$$V_i = X_i\left\{R_1 + i\left(L_1 p - \frac{1}{C_1 p}\right)\right\},$$

$$V_0 = Ee^{ipt} - X_0\left\{R_0 + i\left(L_0 p - \frac{1}{C_0 p}\right)\right\},$$

where R_1, L_1, C_1, and R_0, L_0, C_0 are the resistance, inductance, and capacity of the receiving and sending instrument respectively.

From the above equations we can obtain the most general expressions for the current and potential at any point on the line which are as follows:

$$X = \frac{Ecp}{2\sqrt{K_1^2 + K_2^2}}\{e[^{\beta\xi}\cos(pt - a\xi + \theta) + e^{-\beta\xi}\cos(pt + a\xi + \theta)]$$

$$+ \sqrt{H_1^2 + F_1^2}\,[e^{-\beta\xi}\cos(pt - a\xi - \varphi + \theta) - e^{\beta\xi}\cos(pt - a\xi - \varphi + \theta]\},$$

$$V = \frac{E\sqrt{a^2 + \beta^2}}{2\sqrt{K_1^2 + K_2^2}}\{e^{-\beta\xi}[\cos(pt + a\xi + \theta + \omega) - e^{-\beta\xi}\cos(pt - a\xi + \theta + \omega)],$$

$$+ \sqrt{H_1^2 + F_1^2}\,[e^{\beta\xi}\cos(pt - a\xi - \varphi + \theta + \omega)$$
$$+ e^{-\beta\xi}\cos(pt + a\xi - \varphi + \theta + \omega)]\},$$

where

$$a = \sqrt{\tfrac{1}{2}}\sqrt{cp\{\sqrt{P^2L^2 + R^2} + pL\}}, \quad \beta = \sqrt{\tfrac{1}{2}}\sqrt{cp\{\sqrt{P^2L^2 + R^2} - pL\}},$$

$$\tan\theta = \frac{K_1}{K_2}, \quad \tan\varphi = \frac{H_1}{F_1}, \quad \tan\omega = \frac{\beta}{a}, \quad \xi = l - s,$$

$$H_1 = \frac{Cp}{a^2 + \beta^2}\left\{-a\left(L_1 p - \frac{1}{C_1 p}\right) + \beta R_1\right\},$$

$$F_1 = \frac{Cp}{a^2 + \beta^2}\left\{\beta\left(L_1 p - \frac{1}{C_1 p}\right) + aR_1\right\},$$

$$H_1^2 + F_1^2 = \frac{C^2p^2}{a^2 + \beta^2}\left\{\left(L_1 p - \frac{1}{C_1 p}\right)^2 + R_1^2\right\}.$$

If we consider only the receiving apparatus, then

$$K_1 = \frac{e^{\beta l} + e^{-\beta l}}{2}\left\{-a\sin al - Cp\left(L_1 p - \frac{1}{C_1 p}\right)\cos al\right\}$$

$$+ \frac{e^{\beta l} - e^{-\beta l}}{2}\left\{\beta\cos al + CpR_1\sin al\right\},$$

$$K_2 = \frac{e^{\beta l} + e^{-\beta l}}{2}\left\{ -\beta \sin \alpha l + CpR_1 \cos \alpha l \right\}$$

$$+ \frac{e^{\beta l} - e^{-\beta l}}{2}\left\{ \alpha \cos \alpha l - Cp\left(L_1 p - \frac{1}{C_1 p} \right) \sin \alpha l \right\}.$$

Taking account of the sending apparatus makes the expressions for K_1 and K_2 much more complicated, and they are given in the complete paper which will soon be published.

When $s = l$, that is at the receiving end of the line, we have

$$X_l = \frac{Ecp}{\sqrt{K_1^2 + K_2^2}} \cos (pt - \theta),$$

$$V_l = \frac{Ecp \sqrt{\left(L_1 p - \frac{1}{C_1 p} \right)^2 + R_1^2}}{\sqrt{K_1^2 + K_2^2}} \cos (pt - \varphi - \theta - \omega).$$

In calculating the value of X_l as given by the above equation I have assumed three distinct cases: (1) The terminal apparatus neglected entirely, (2) the receiver included in circuit, and (3) the receiver in series with a condenser in circuit.

I have assumed three distinct frequencies, 500, 1,000 and 1,500, and two different lines, one 30 km. long and one 300 km. long.

The constants of 30 km. line (Cable, 19 B. S.) are approximately as follows:

$L = .00001$ henry per km.,
$C = 0.045$ microfarad,
$R = 27.5$ ohms.

Using these constants and assuming that the impressed voltage corresponding to the frequencies 500, 1,000, 1,500, are E_1, E_2, E_5 respectively, we shall have the following table.

	Frequency = 500.	Frequency = 1,000.	Frequency = 1,500.
Case 1, no terminal apparatus.	$X_l = 0.00114 E_1$	$X_l = 0.00099 E_3$	$X_l = 0.00089 E_5$
Case 2, receiver in circuit.	$X_l = 0.00176 E_1$	$X_l = 0.005 E_3$	$X_l = 0.0046 E_5$
Case 3, receiver and a condenser of 1.5 m.f. in circuit.	$X_l = 0.0018 E_1$	$X_l = 0.0019 E_3$	$X_l = 0.0045 E_5$

An examination of the above table shows that the receiver in the circuit increases the distortion, and it is further seen that the introduction of a condenser will improve the transmission.

Now while telephoning at such short distance is possible with almost any apparatus, yet it will be admitted that there is considerable room for

improvement, and it would seem that the introduction of a condenser of the proper magnitude in series with the receiver ought to produce good results.

To show the effect on the distortion in long distance transmission, I have made similar calculations for a cable (13 B. S.) 300 km. long. The electrical constants of such a cable are approximately as follows:

$L = 0.0001$ henry per km.,
$C = 0.045$ microfarad per km.,
$R = 7$ ohms per km.

Using these values and the constants of the receiver the same as in the previous case, we get the the following table:

	Frequency = 500.	Frequency = 1,000.	Frequency = 1,500.
Case 1, no terminal apparatus.	$X_l = 0.003 E_1$	$X_l = 0.00011 E_3$	$X_l = 0.000053 E_5$
Case 2, receiver in circuit.	$X_l = 0.00126 E_1$	$X_l = 0.00017 E_3$	$X_l = 0.000045 E_5$
Case 3, receiver and a condenser of 1.5 m.f. in circuit.	$X_l = 0.0014 E_1$	$X_l = 0.0002 E_3$	$X_l = 0.00005 E_5$

From the table it can be seen that the introduction of the telephone receiver does not materially influence telephonic transmission.

AN ELECTRODLESS METHOD FOR MEASURING THE CONDUCTIVITY OF ELECTROLYTES.[1]

BY LOUIS COHEN.

IF we insert a tube filled with an electrolyte into a solenoid, and then pass an alternating current through the winding of the solenoid, eddy currents will be generated in the electrolyte which will heat the electrolyte and thus consume a certain amount of energy.

Let us suppose now that the solenoid forms one arm of a Wheatstone bridge, through which we pass a high frequency current, and let us determine its resistance with and without the electrolytic core, there evidently will be a difference in the two measurements, for the loss of energy in the electrolyte due to the eddy currents will effect the measurement as if an additional resistance was inserted in that arm of the bridge. Now it is quite evident that the energy loss in the electrolyte will be proportional to its conductivity, hence the change in resistance measured in the bridge will be proportional to the conductivity of the electrolyte. If we could obtain a mathematical relation between these two quantities, we shall have, what seems to be, a very simple method for the determination of the conductivity of electrolytes without the use of electrodes.

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1908.

I have worked out the mathematics of the problem and I find the following relation obtains:

$$R = 2\pi^3 \lambda p^2 n^2 l a^4,$$

$$\lambda = \frac{R}{2\pi^3 p^2 n^2 l a^4},$$

where R denotes the increase in resistance (measured),
p denotes $2\pi \times$ frequency,
n denotes number of turns per cm.,
l denotes length of electrolytic core,
a denotes radius of electrolytic core.

As to the magnitude of the quantity R, we can readily see from the following example. Suppose $\lambda = 10^{-9}$, $p = 2\pi \times 10^4$, $n = 10$, $l = 50$ cm., $a = 7$ cm. Then $R = (2\pi^3 \times 10^{-9} \times 4\pi^2 10^8 \times 10^2 \times 50 \times (49)^2/10^9)$ $= 3$ ohms approximately. The resistance of the winding of the solenoid calculated by the formula given in my paper[1] "The Influence of Frequency on the Resistance and Inductance of Solenoidal Coils" is found to be about 55 ohms. The change in resistance will therefore be about six per cent., of sufficient magnitude to be determined with considerable accuracy.

What is the Most Important Portion of a Thermoelement.[2]

By Walter P. White.

ALONG a thermoelement as ordinarily used, there are three temperature regions; one, fairly constant, at each end, and an intermediate *gradient region* where the temperature changes from one of the end values to the other. (In an element used with a cold junction in ice, there are usually two such temperature systems in series.) The present paper applies only where this temperature distribution exists. In such cases, applying the formula for electromotive force of a thermoelement which is not perfectly homogeneous,

$$E = \int \theta dH$$

(θ, temperature, H, thermoelectric power, E, electromotive force), it is easy to show that, except for second order corrections: (1) the temperature measured is that of the junction; (2) but it is measured in terms of thermoelectric power of that part of the thermoelement which passes through the gradient region of temperature, and not of that lying ~~near~~ the junction; (3) inhomogeneities, permanent or temporary, in the other portions are much less important than in the gradient region.

[1] Bulletin of the Bureau of Standards, Vol. 4, p. 161.

[2] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1908.

This conclusion is little more than an extension of the well-known rule that solder or other foreign material at the junction affects the electromotive force but little. Nevertheless, it seems worth stating, both on account of its importance and because much in the literature seems to point to a very different conclusion and to emphasize the importance of the (usually) really unimportant portion of the thermoelement near the junction.

The following practical conclusions follow:

1. In selecting wire for a thermoelement, the gradient portion is the only part where great care needs to be exercised. The production of a good thermoelement is thus easier than has sometimes appeared.

2. If an inhomogeneous element is shifted to a different depth in the bath or furnace, it (in general) at once becomes a different element. The effect of a change in the material near the junction, however, is much less important.

3. In amputating a contaminated platinum thermoelement to restore its original value, it is usually practically sufficient to cut off only enough so that fresh uncontaminated wire occupies the gradient region.

Commercial constantan wire has been obtained whose original variations in thermoelectric power were 0.001 of the electromotive force against copper. By suitable selection and combination of this wire, thermopiles were easily constructed good to one part in one hundred thousand, that is, .001 of a degree at 100°. These even showed no variation in reading equal to .001 of a degree when the depth of immersion in a constant temperature bath at 100°, and therefore the position of the gradient region, was varied several centimeters.

SPECIFIC HEATS AT HIGH TEMPERATURES.[1]

BY WALTER P. WHITE.

THE substances under examination were dropped from an electric resistance furnace into the calorimeter described a year ago. The errors of the calorimeter were negligible. The loss of heat in the air was eliminated by first determining the heat given out by an empty platinum crucible at various temperatures and then subtracting this as an empirical correction from the total heat of crucible and included material. The empty crucible was weighted with platinum so as to keep constant conditions with regard to the splash, etc. The total loss of heat of the crucible alone (and this includes also the slight loss from the formation of steam as the crucible strikes the water) was only 4 per cent. The crucible was dropped electrically (Harker's method) by melting a supporting wire. This was done automatically by the swinging aside of a shield between furnace and calorimeter. The principal source of error (1 per cent. or more) was found in the uncertain tem-

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1908.

perature distribution within the furnace; a longer and narrower furnace is expected to diminish this. The accidental errors averaged about .3 per cent., that is, duplicate results usually agreed as well as this.

The Application of the Ionization from Hot Bodies to Thermometric Work at High Temperatures.[1]

By O. W. Richardson.

THE paper directs attention to the possibilities of the phenomena exhibited by the emission of ions by hot bodies for the determination of high temperatures in the absolute scale. Two methods of attacking this problem are outlined, which are independent of one another as regards their theoretical foundations. The theoretical and practical advantage of the two methods are discussed.

Resonance Spectra of Sodium Vapor.[1]

By R. W. Wood.

SODIUM vapor has a banded absorption spectrum comprised between wave-lengths 4,500 and 5,700 and extending from wave-length 580 far out into the infra-red, probably to 15 or 20 μ. There are between five and six thousand lines in the banded spectrum in the blue-green region. If the non-luminous vapor of the metal, contained in a steel tube is illuminated with white light, it emits a brilliant green light (fluorescent) which appears to be the exact compliment of the absorption spectrum. If, however, monochromatic light is thrown into the vapor, the spectrum of the emitted light consists of isolated bright lines, separated by intervals of about 38 Ångström units. In many cases the wave-length interval is remarkably constant, not varying by more than one or two tenths of a unit. If we excite the vapor with the light of the magnesium arc (green triplet "b") the emission spectrum of the vapor shows the triplet repeated a number of times at regular intervals. Since bright line spectra obtained in this way appear to be radically different from spectra obtained by any other means, I propose that they be designated *resonance spectra*, since they are without doubt the result of resonance vibrations set up within the molecule by the absorption of light of a single periodicity. Similar spectra have been obtained with the vapor of potassium, and probably other metallic vapors will show the phenomenon as soon as we learn how to handle them. Excitation of the sodium vapor with the light of the lithium arc gives a beautiful series of lines in the red and orange region as well as in the green and blue (slide shown). During the past winter these resonance spectra have been photographed over again with a con-

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1908.

cave grating of 14 feet radius, which enables us to determine the wave-lengths of the bright lines in the series to within 0.1 A.U. This work has been done in collaboration with Mr. Felix Hackett, fellow of the Royal University of Ireland.

The apparent absence of polarization in the light emitted when the vapor is excited by white light has always appeared to me to be difficult to reconcile with the theory that the radiation is directly reëmitted by the resonating electrons. On making a more critical examination I have recently found that in a direction making an angle of 90° with that of the exciting beam, the fluorescent light is partially polarized, even when the exciting light is unpolarized. The amount of polarization is about 15 per cent. when the incident light is unpolarized and 30 per cent. when a polarized excitation is used. It is clear that the vibrations in the exciting light which are parallel to the direction in which the fluorescent light is emitted, will, on the most elementary theory of the phenomenon which we can form, excite a vibration which cannot send out transverse waves in the direction specified. In other words the electrons will be moving in the line of sight. Or putting it in another way, if the electrons are free to move in any direction, the incident beam cannot excite vibration parallel to the direction in which it is travelling. On this theory we should expect complete polarization of the reëmitted light. That only about 15 per cent. is polarized can perhaps be explained by assuming that we are dealing with constrained motion. If an electron could only vibrate along a straight line the position of which within the molecule was fixed, vibrations would occur for all positions of the line except one (parallel to the incident beam) and these vibrations would in general have a component parallel to the incident beam. It is also possible that rotation of the molecules and collisions with neighboring molecules may exert a depolarizing action. The matter is under investigation at the present time. The presence of 11 per cent. of polarized light in the solar corona makes a fluorescence theory of the corona plausible.

INTERFERENCE OF LIGHT IN CHLORATE OF POTASH LAMINÆ.[1]

BY R. W. WOOD.

CRYSTAL plates have been obtained which reflect metallically a band in the spectrum less than 15 Ångström units in width, or less than three times the distance between the *D* lines. Photographs of the spectrum of the light transmitted through the crystal, showing the corresponding dark band were shown. Such crystals must contain six or seven hundred parallel twin planes only half a wave-length apart.

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1908.

On Diffuse Reflection of Infra-Red Energy.[1]

By A. Trowbridge.

A STUDY of reflection from powders of transparent materials to size of the particle being of the same order of magnitude as the wave-length of the reflected energy.

Powders of fluorite, sylvite, rock salt and sulphur show a slight increase in diffuse reflection with increasing wave-length.

Powdered quartz shows marked "body colors" in the region where the crystal shows only slight absorption and a marked "surface color" in the region where the crystal begins to absorb strongly.

The Infra-Red Absorption and Reflection of Collodion.[1]

By A. Trowbridge.

A STUDY of the optical properties of collodion undertaken with the object of determining whether it would prove a suitable substance with which to coat rock salt surfaces in order to preserve polished surfaces.

The extinction coefficient of collodion is practically negligible in the region between the visible spectrum and $\lambda = 6\,\mu$. In this region a rock salt plate or prism is more transparent when coated with a thin film of collodion than it is without being coated.

In the region from $6\,\mu$ to $10\,\mu$ there are two narrow absorption bands and one extended region of absorption for all of which the extinction coefficient attains values great enough to cause well-marked surface color.

The Absorption and Reflection of Calcite and Aragonite for Infra-Red Rays as Dependent upon the Plane of Polarization.[1]

By R. E. Nyswander.

CLEAR polished crystal sections, cut to contain the principal directions of vibration, were investigated with polarized light for absorption and reflection. A Nernst heater furnished the source of energy which was polarized by reflection from a smooth selenium surface. A reflecting spectrometer employing the method of constant angle of emergence was used. Energy was measured with a radiometer. Reflecting power was compared with that of silver, which was assumed total.

The absorption band in calcite at $11.3\,\mu$ was found to be due to complete absorption of the extraordinary ray, the ordinary ray showing no trace of an absorption band in this region. The band at $14.1\,\mu$ occurs in both rays, but to a small extent in the extraordinary ray, while for the

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1908.

ordinary ray absorption is complete. Bands of metallic reflection are present at both of these points.

The reflection from aragonite as dependent upon the plane of polarization for the three principal directions of vibration shows that the band of metallic reflection at 11.55 μ is due to the reflection of one ray, and for this ray the reflection is nearly equal to that of silver. The two other directions of vibration show no increase in reflecting power through this region. In the region of 14.1 μ reflection bands are present for each direction of vibration. The direction showing the smallest reflecting power between 11 μ and 12 μ reflects most copiously at the second band, reflecting 29 per cent. of the incident energy. Two of these bands occur at 14.1 μ, the other is shifted to 14.2 μ.

A STUDY OF PHOTO-ELECTRIC CELLS CONTAINING A FLUORESCENT ELECTROLYTE.[1]

BY PERCY HODGE.

THE above mentioned cells have been investigated by the writer in three different series of experiments. The original object of the work was to determine whether there is a change of conductivity of a fluorescent solution when under the influence of the exciting light. The solutions used were both dilute and concentrated, the solvent being absolute alcohol. The exciting light was an arc lamp, and the resistance measurements were made with an ordinary Wheatstone's bridge and galvanometer, as being more sensitive than any of the alternating current apparatus used for measuring resistances of solutions. The conclusion arrived at was that in the cells investigated, if the electrodes are entirely concealed from the light, or if the liquid is kept rapidly moving past the electrodes, no change is produced as great as 0.1 per cent. when the liquid is illuminated.

The second stage in the experiments was an investigation of the effect of illuminating anode and kathode in turn, changing the potential difference at the terminals of the cell from 0.2 volt, by small stages up to 3.6 volts. Very large changes in apparent resistance were observed when the potential differences were small, the effect at kathode being to greatly decrease the resistance, that at anode to increase it in about the same amount. As the potential differences became greater these effects became less, and finally the effect on the kathode became an increase of resistance and that at anode a decrease. Of these latter effects that at kathode was much the greater. Finally both effects were lost at about 3.5 volts.

The last work which has been done grew out of results of the last ex-

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1908.

periments, and has been a study of photo-active effects produced by illuminating one electrode only, no external electromotive force being applied. This effect, in the case of a number of fluorescent substances which have strong absorbing power, has been found quite large, the electromotive force produced reaching a maximum of between two and three tenths of a volt, near the infra edge of the absorption band, falling off abruptly as the electrode leaves the absorption band on the infra side, and much more gradually toward the violet. In all cases thus far observed when alcoholic solutions were used the exposed electrode became positive to the unexposed. One cell has been tried with fluorescein in water solution as the electrolyte, in which the effect was of opposite sign. The writer expects to publish in a short time a more extended account of his work, in which curves will be included to illustrate the above phenomena.

The Principles Involved in the Selection and Definition of the Fundamental Electrical Units to be Proposed for International Adoption.[1]

By F. A. Wolff.

In the paper the work of the next International Electrical Congress was briefly outlined. Especial stress was laid on the question of the choice of the fundamental units as will be seen from the summary of the conclusions which follow:

1. The decisions of the Berlin Conference of 1905 should not be regarded as binding in view of the large amount of work since published on the silver coulometer and standard cell.

2. The international electrical units to be adopted should be regarded as separate and distinct from the absolute units on which they were originally based.

3. The choice between the ampere and the volt should be made exclusively on the basis of merit.

4. That the principles on which the decision should be made are

a. Accuracy of reproduction from specifications.

b. Concreteness.

c. Ease of reproduction.

5. The accuracy of reproduction of the coulometer remains to be established, as coulometer measurements made by different investigators establish only relative accuracy, no accurate comparisons of the results obtained by different investigators having thus far been made.

6. If a decision must be at the present time and on the basis of merit, the cell should be selected on account of the advantages it offers from the

[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 24–25, 1908.

standpoint of concreteness and ease of reproduction, since no greater accuracy of reproduction can be claimed for the coulometer in the light of the data at hand. In addition this choice is more logical from the standpoint of the standardizing laboratory as it leads to fundamental units corresponding to the standards submitted for certification as well as corresponding to the methed employed for measuring currents in terms of standards of resistance and electromotive force.

7. In view of the preference indicated for the coulometer at the Berlin Conference, the reproducibility of the cell and coulometer should, however, first be definitely established by systematic international coöperation, which would also result in bringing to light unrecognized defects in the specifications proposed.

8. If the ampere is defined in terms of the coulometer, the value to be taken for the standard cell and which must be depended on between coulometer measurements, must be determined at each of the national standardizing institutions, the results obtained reduced to a common basis by exchange of cells and resistance standards, and a mean value taken to insure international uniformity.

Unless the accuracy of the result, involving errors in the realization of both the ohm and ampere is greater than that attainable in the reproduction of the cell from specifications, the definition of the ampere will subsequently be ignored, making the cell in effect a primary standard. The same result can be more directly obtained by selecting the volt as the second fundamental unit since a practically equivalent value may be assigned to the cell, in which case the corresponding value for the electrochemical equivalent of silver need not be known to the highest accuracy, as it could only be used for the purpose of loosely defining the ampere.

NEW BOOKS.

Vorlesungen über theoretische Spektroscopie. Von A. GARBASSO. Pp. viii + 256. Barth, Leipzig, 1906.

Professor Garbasso's book emphasizes in the most striking way the ground that has been traversed in this important department of optics within the last decade. The thirty years which followed the great work of Bunsen and Kirchhoff were spent chiefly in the accumulation of experimental data and the bewildering wealth of material amassed testifies to the industry and enthusiasm of the army of spectroscopists who entered the new domain.

This series of lectures deals with the explanation of those portions of optics, such as anomalous dispersion, selective absorption, surface color, optical resonance, the occurrence of spectral series and of double and triple lines, the Zeeman effect, etc., which lay beyond the range of the older theories. The explanation has its foundation in the electro-magnetic theory, into the terms of which the Helmholtz theory is translated. From the author's experiments on electro-magnetic resonance to the work of Rubens, E. F. Nichols and Aschkinass and thence to optical resonance in the visible spectrum, the steps are obvious. After the development of these relations the author proceeds in the later and more important chapters to the consideration of the behavior of various combinations of pendulums and from this he leads up to the construction of models corresponding to the molecules of complex compounds and to a general mechanical theory of the phenomena of radiation.

E. L. N.

Lehrbuch der Experimentalphysik. By ADOLPH WÜLLNER. Band 1. Allgemeine Physik und Akustik. 6th Edition. Revised by A. Wüllner and A. Hagenbach. 8vo. Pp. xiv + 1058. Leipzig, B. G. Teubner, 1907.

It is a pleasure to note the appearance of a new edition of this valuable reference book. The first volume, covering the field of General Physics and Acoustics, has been revised so as to include the more recent work up to the beginning of the year 1907. References to original articles are numerous and a complete index makes it easy to look up any particular topic.

At the present time there appears to be no work in English which is to be regarded as the equivalent of the general treatises like that of Wüllner which have appeared in Germany and France. When one considers the enormous amount of work involved in the preparation of such a work it is not surprising that no one has been found to carry out the task. It is to be hoped, however, that an English translation of one of these general treatises may some time be undertaken, for it is unfortunate that so useful a book should not be available for all workers in physics in this country instead of for those only who are familiar with German.

E. M.

A Laboratory Guide for Students in Physical Sciences. By H. SCHAPPER. Pp. v + 61. New York, John Wiley & Sons, 1908.

The purpose of this little volume is explained by the following extract from the preface: "The student of physics cannot handle the results of his measurements in the laboratory and has no conception of the accuracy of his work without a course in precision of measurements. Between the meager information usually given on the subject in laboratory manuals and elaborate treatises on the adjustment of observations there is a considerable gap. This text-book is intended to fill the lacuna."

The book contains chapters on Units and Dimensions, Discussion of Results and Graphical Representation, Approximation Formulæ, Adjustment of Observations, Effect of Errors of Observation on the Result, and similar topics.

Mathematical Handbook containing the Chief Formulas of Algebra, Trigonometry, Circular and Hyperbolic Functions, Differential and Integral Calculus, and Analytical Geometry, together with Mathematical Tables. By EDWIN P. SEAVER. Pp. viii + 179. New York, McGraw Publishing Company, 1907.

This is a well selected and carefully arranged collection of formulas and tables which should be extremely useful to physicists, engineers and mathematicians. It is only by extended use that the full value of such a handbook can be ascertained and appreciated; but a small acquaintance with the book is sufficient to show that those who use it will have a growing appreciation of their indebtedness to the author for its compilation.

Alternating Current Motors. By A. S. MCALLISTER. Second edition. Pp. xi + 291. New York, McGraw Publishing Co., 1907.

At no too frequent intervals a book appears which is a distinct contribution to knowledge, on account of the original material it contains and the soundness of its treatment. Such a book is the one in hand which treats in a thorough manner the various types of alternating current motors. The reader is supposed to have a general knowledge of alternating currents.

An occasional blemish is the involved sentence at times indulged in. This appears in parts of the book taken without sufficient revision from earlier papers by the author, and not at all in the new matter of the second edition. In an excess of effort to avoid ambiguity, the author has overworked such expressions as *time-phase* and *electrical-space-quadrature* in places where *phase*, *space-quadrature*, etc., would be sufficient.

Besides minor changes, the second edition contains a discussion of the interesting motor-converter, a chapter on leakage reactance and a well written supplement on the synchronous motor. This last is, we believe, the best discussion there is of the synchronous motor. A system of circular loci is developed, somewhat analogous to the circle locus for the induction motor, making possible a treatment both simple and adequate.

B.

Electrical Energy; its Generation, Transmission and Utilization. By E. J. BERG. Pp. xi + 184. New York, McGraw Publishing Co., 1908.

This, like the foregoing, is an authoritative book. Very nearly all the theory of polyphase alternating current is introduced and elucidated with reference to one concrete problem, namely, to transmit certain power, a certain distance for certain purposes. As applied to this problem, the author discusses inductance and capacity, both distributed and localized, skin effect, corona, resonance, wave form and harmonics, transformers, alternators, etc. The treatment is vivid for the theory is applied in every case to the problem at hand.

B.

An Introduction to the Study of Electrical Engineering. By HENRY H. NORRIS. Pp. 404. New York, John Wiley & Sons, 1907.

This book is entirely descriptive, written from the point of view that a student should have a knowledge of things and phenomena before any reasons can be ascribed to them. The writer states in the preface that electrical engineering is not a separate profession but is becoming more and more a component part of mechanical engineering, and the book is written from this standpoint. The book gives the student an introductory knowledge of the whole field of electrical engineering; it is assumed that more specialized knowledge will be gained in subsequent courses.

The writer has succeeded admirably in dealing with the side of the subject which he has selected.

Electric and Magnetic Measurements and Measuring Instruments. By FRANK W. ROLLER. Pp. v + 398. New York, McGraw Publishing Co., 1907.

This book is useful for laboratory reference; it is not adapted as a text book and it is doubtful if, outside of the laboratory, it will be of

use to many engineers. Its real value lies in its full description of instruments, historic and modern; the description of methods is less satisfactory being often inadequate and without reference to original sources.

Laboratory Work in Electrical Engineering, Preliminary Grade. By JOHN ROBERTS, JR. Pp. x + 218. New York, D. Van Nostrand Company, 1906.

The scope of this book is partly in the field of electrical (physical) measurement and partly in the field of electrical engineering; and for some places, as the laboratory for which it was written, it may be well suited. For other places it may be found not to cover sufficiently either field. The chapter headings are: Graphical Representation of Experimental Results, Verification of Ohm's Law, Measurement of Resistance, Measurement of E.M.F., Measurement of Current, The Potentiometer, Calibration of Electrial Measuring Instruments, Miscellaneous Experiments.

Under miscellaneous, are twenty-eight experiments in electrical engineering, which appears to be too much "preliminary," considering that they are all elementary and a wide field including all of alternating currents is still uncovered. It will seem to many that engineering students should devote their attention to experiments involving fundamental principles on the one hand and engineering methods on the other, without spending too much time on intermediate ground.

Standard Handbook for Electrical Engineers. By a Staff of Specialists. Pp. xx + 1283. New York, McGraw Publishing Co., 1908.

The material of this book is the best of its class; the mechanical workmanship the worst. Type, illustrations and press work are poor, giving the appearance of the *n*th edition from hand-me-down plates. This is the more unfortunate on account of the great value of the subject-matter; the reviewer finds he must keep a copy on his desk and refers to it daily. The various sections covering the whole field of electrical engineering are prepared by specialists and contain a wealth of material; a great deal of this is new in a book of this kind and not quickly found even in a good library. Particularly is this true of alternating current transmission and apparatus. The arrangement and indexing is good and the different parts of the book are well harmonized. As the treatment of many subjects is necessarily brief, a reference in each case to an authoritative book or article would add enormously to the value of such a handbook.

B.

Abhandlungen über Theoretische Physik. Band 1, Erste und zweite Lieferung. By H. A. LORENTZ. Leipzig, Teubner, 1907. 8vo, pp. 489.

The author has taken advantage of the opportunity afforded by the republication of his papers in collected form to revise the form of presentation to some extent, and to introduce greater unity in the mathematical treatment and use of symbols. The papers have been arranged with reference to the subjects treated, and with little regard to their chronological order. Thus we find first a discussion of "The Principles of Dynamics," suggested by Hertz's "Prinzipien der Dynamik," and first published in 1902; after this two articles on "Die Bewegung einer reibenden Flüssigkeit," and "Die Entstehung turbulenter Flüssigkeitsbewegungen," which appeared in 1896–7; and next a paper on "Les Equations du Mouvement des Gaz et la propagation du son suivant la théorie cinétique des gaz," dated 1881. The use of either one of three languages, no one of them his own, apparently with equal facility, and certainly with a style that is always clear and pleasing, is something that will fill most American readers with envy.

The first part of the present volume is devoted to questions connected with dynamics and thermodynamics. In addition to the papers referred to above mention may be made of papers on Boltzmann's Virial theorem, on the Entropy of a Gas, the Second Law of Thermodynamics, the Molecular Theory of Dilute Solutions, the Distribution of Kinetic Energy among the Molecules of a Gas; and, as an illustration of the field covered, a paper on "Die Grösse von Gebieten in einer n-faction Mannigfaltigkeit."

The second part of the first volume contains two articles on crystal symmetry and the bounding surfaces of crystals. This section is however chiefly devoted to problems connected with optics and to papers dealing with the problem of the relative motion of the earth through the ether. The following titles may, for example, be cited: "Stokes' Theory of Aberration"; "Die Fortpflanzung des Lichtes in einem sich bewegunden Medium"; "Sur la méthode du miroir tournant pour la détermination de la vitesse de la lumiére"; "Die relative Bewegung der Erde und des Aethers."

It will be noticed that the papers contained in this first volume refer to numerous questions that have recently been the subject of very interesting discussions. The delightfully clear and illuminating manner in which such questions are treated by Professor Lorentz makes these papers invaluable to the specialist and extremely interesting to the general physicist. E. M.

Lehrbuch der Thermodynamik in ihrer Anwendung auf das Gleichgewicht von Systemen mit gasförmig-flüssigen Phasen. Erster Teil. By J. D. VAN DER WAALS. Erster Teil. Bearbeitet von Dr. Ph. Kohlstamm. 8vo, pp. xii + 287. Leipzig and Amsterdam, Maas and Van Suchtelen, 1908.

The main title of Professor van der Waal's work is misleading in that it suggests a general treatise on Thermodynamics, whereas in reality no attempt is made in the book to cover the whole field. On the other hand the subtitle, which apparently restricts the discussion to the application of thermodynamics to systems containing liquid and gaseous phases, is perhaps even more misleading, since it implies a narrowness of scope that is not justified either by the list of topics given in the table of contents or by the method of treatment in individual cases.

The book is based upon lectures delivered by Professor Van der Waals at the University of Amsterdam and has been prepared for the press by one of his former students, Dr. Kohlstamm. The treatment is naturally more complete in those branches of the subject to whose development the author's own investigations have contributed. Thus the equation of state which bears the author's name is used in place of the equation of an ideal gas more frequently than is common in books on thermodynamics; and the thermodynamic theory of capillarity is given more than usual prominence. The fact that an authoritative and connected account is given of the author's important work in the domain of thermodynamics makes the book of especial interest and value. The subject of thermodynamics is one of such peculiar difficulty and has so many widely differing aspects that it seems impossible for one who is not himself an investigator in this field to prepare a satisfactory treatise on the subject. But a treatise written by a specialist is almost of necessity more or less one sided. Compare for example the three or four treatises on thermodynamics by the leading workers in this field. No one would call these works narrow; and the term one-sided also does not seem wholly appropriate. But the point of view and methods of treatment are so widely different that it sometimes seems as though there was nothing but a skeleton in common. In thermodynamics, more than in any other branch of physics, it is necessary to consult a number of different authorities in order to obtain a broad view of the subject. The addition of Professor Van der Waal's lectures to the list of treatises available for this purpose is a subject for congratulation.

The present volume is divided into four sections entitled respectively: "Der erste Hauptsatz und seine Anwendungen"; "Der Zweite Hauptsatz und seine Anwendungen"; "Das Allgemeine Gleichgewichtsprinzip und seine Anwendungen"; "Thermodynamische Theorie der Kapillarität." A second volume is to appear later. E. M.

The Study of Stellar Evolution. An Account of Some Recent Methods of Astrophysical Research. By GEO. E. HALE. 8vo, pp. xi + 252 and 104 plates. Decennial Publications of the University of Chicago. University of Chicago Press, 1908.

The plan and scope of this very interesting book will be best explained perhaps by the following extracts from the preface:

"As first planned, this book was intended to serve as a handbook to the Yerkes Observatory. Many inquiries regarding the observatory's work, made by the numerous visitors received there annually, seemed to call for a printed explanation of the purposes in view and the observational methods employed. Removal to California and new duties connected with the organization of the Mount Wilson Solar Observatory caused a modification of the project. I finally adopted the plan of describing a connected series of investigations, laying special stress on the observational methods employed, in the hope of explaining clearly how the problem of stellar evolution is studied. The advantage of using concrete illustrations drawn, in large part, from personal experience, and the desire that the book should be of special service to visitors at the Yerkes and Mount Wilson Observatories, are sufficient reasons, I trust, for the otherwise undue proportion of space devoted to these institutions."

"I have made no attempt to deal with the general problem of stellar evolution, or to offer anything approaching an adequate description of the observational methods of astrophysics. The various researches described are chosen rather arbitrarily, in some cases with more regard for my personal acquaintance with the facts than because of their intrinsic importance. I trust, however, that although this method of treatment has necessarily resulted in a fragmentary exposition of the subject, the book will serve to show how the problem of stellar evolution is attacked along converging lines, leading from solar, stellar, and laboratory investigations."

The book is one that does not require great technical familiarity, either with astronomy or with physics, and may be put in the hands of one having only a general knowledge of these subjects with the certainty that by far the greater part of the book can be read with interest and understanding. For the physicist, however, and especially for one who has had experience with the difficulties and the charm of the experimental side of his subject the book possesses a fascination that is quite unusual. The author writes of problems to whose solution he has himself made important contributions, of instruments which he has designed, or of investigations with which, owing to his acquaintance with other astrophysicists, he has a thorough personal familiarity. This fact, together with the pleasing style and complete absence of any trace of egotism, gives to the book a character and charm that are rarely met with.

The book contains at the end over one hundred full page plates, in all cases excellent photographic reproductions. Views of observatories are given, and of particular pieces of apparatus; numerous photographs of the sun, of prominences, sun spots, and flocculi; excellent photographs of star clusters and nebulæ; and an extended series of spectra illustrating the employment of spectroscopic methods in astrophysics. One photograph, which I have not before seen reproduced, gives a portrait of Rowland standing near his famous ruling engine. Several views of the Mount Wilson Solar Observatory and of the surrounding mountains are of great interest and beauty. E. M.

Theorie, Konstruction und Gebrauch der feineren Hebelwage. By Dr. W. FELGENTRAEGER. 8vo, pp. vi + 310. Leipzig and Berlin, Teubner, 1907.

The theory of the balance and the conditions to be met in the design of the different parts are discussed in great detail and by one whose experience in this field has been unusually extensive. The work is well illustrated by explanatory diagrams and by numerous photographs of complete balances and of individual parts. While the whole work will prove of the greatest value to the specialist the general physicist will probably be chiefly interested in the description of the types of balance that are suited for particular kinds of work and in the discussion of the proper conditions for their use.

Kleiner Leitfaden der praktischen Physik. 2d Edition. By F. KOHLRAUSCH. 8vo, pp. xviii + 268. Leipzig, Teubner, 1907.

Based upon the author's well known "Leitfaden der praktischen Physik," of which the present volume is an abbreviated edition, the book is intended for beginners in the laboratory, and especially for those who do not intend to specialize in physics. The appearance of a second edition indicates that it has been appreciated. In this country the language unfortunately prevents the use of the work as a text-book. But either this book or the original more complete "Leitfaden" is doubtless present as a reference book in almost every laboratory in the country.

Les Découvertes Modernes en Physique. By O. MANVILLE. Pp. 186. Paris, Libraire Scientifique A. Hermann, 1908. (*Received.*)

Immunochemistry. The Application of the Principles of Physical Chemistry to the Study of the Biological Antibodies. By SVANTE ARRHENIUS. Pp. ix + 309. New York, The Macmillan Company, 1907. (*Received.*)

Die Milchstrasse. By MAX WOLF. 8vo, p. 48. Leipzig, Barth, 1908.

This pamphlet gives the text of an address by Professor Wolf before the Dresden meeting of the Naturforscher und Ärzte in 1907. It contains a description, popular in the best sense of the word, of the many interesting features of the Milky Way, illustrated by numerous excellent reproductions from photographs.

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